1

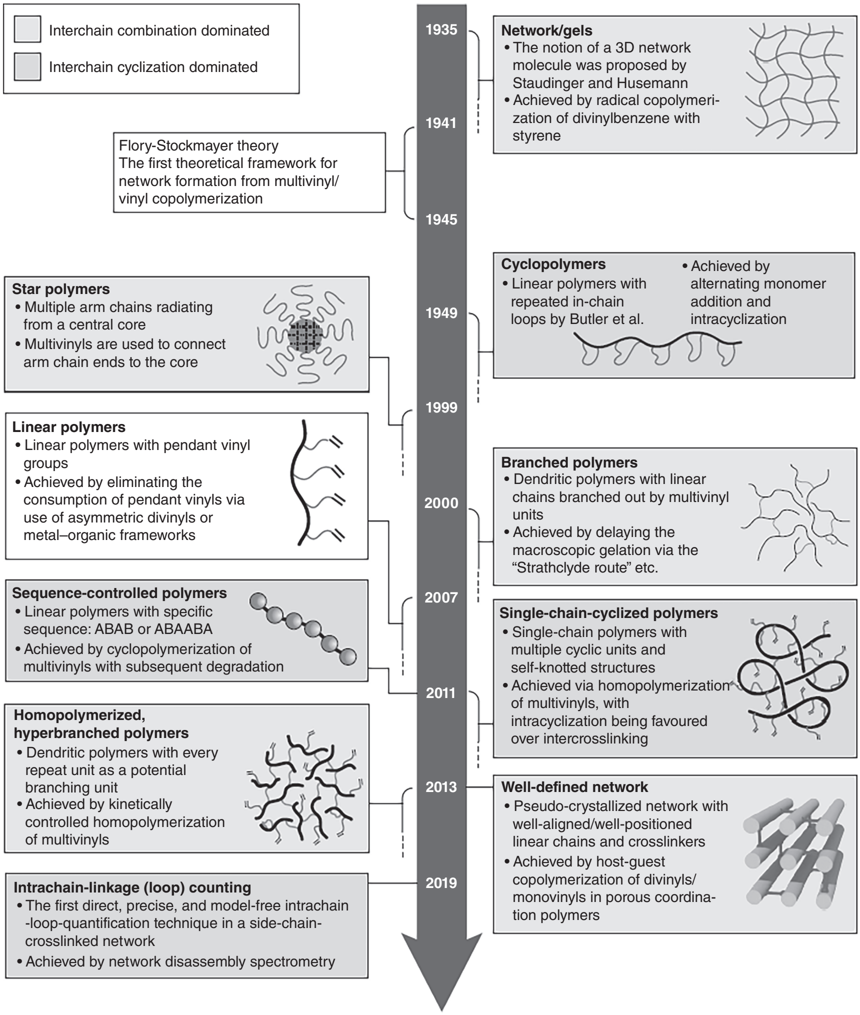
Origin of Polymer Materials

1.1 History of Polymers

A polymer is an organic compound, natural or synthetic, with a high molecular weight made up of repetitive structural units. Large-size chains are formed from the covalent union of various monomer units [1]. A single-polymer molecule may consist of hundreds to a million monomers and may have a linear, branched, or network structure. Polymeric solid can be thought of as a material that contains many chemically bonded parts or units which themselves are bonded together to form a solid. The word polymer means “many parts.” Two industrially important polymeric materials are plastics and elastomers. Plastics are a large and varied group of synthetic materials that are processed by forming or molding into a shape. There are many types of plastics, such as polyethylene (PE) and nylon [2]. Elastomers or rubbers can be elastically deformed a large amount when a force is applied to them and can return to their original shape when the force is released. Polymers have many properties that make them attractive to use in certain conditions. Many polymers (i) are less dense than metals or ceramics, (ii) resist atmospheric and other forms of corrosion, (iii) offer good compatibility with human tissue, and (iv) will exhibit excellent resistance to the conduction of electrical current [3]. Covalent bonds hold the atoms in the polymer molecules together and secondary bonds then hold groups of polymer chains together to form the polymeric material [4]. Copolymers are polymers composed of two or more different types of monomers.

Many examples of synthetic polymers have been mentioned; polyesters or nylons are used more than others like the one which is used for medical applications for organs, degradable sutures, etc. [5]. Based on economic and application considerations, plastic materials can be divided into a commodity and engineering plastics. In the first group, PE, polypropylene (PP), and polyvinyl chloride (PVC) are considered, and in the second, polycarbonate (PC), polyether ether ketone (PEEK), polyimide (PI), etc., are considered. Fibers, natural, artificial (modified natural), and synthetic are characterized by high aspect ratio, high strength and modulus, and other properties depending on their applications. Elastomers exhibit the ability to stretch and retract rapidly [6]. The commercial development of this poly-fiber (PF)

Polymer Nanocomposites for Energy Applications, First Edition.
T. Daniel Thangadurai, Manjubaashini Nandhakumar, Sabu Thomas, and Ange Nzihou.



Network/gels
- The notion of a 3D network molecule was proposed by Staudinger and Husemann
- Achieved by radical copolymerization of divinylbenzene with styrene

Flory-Stockmayer theory
The first theoretical framework for network formation from multivinyl/vinyl copolymerization

Cyclopolymers
- Linear polymers with repeated in-chain loops by Butler et al.
- Achieved by alternating monomer addition and intracyclization

Star polymers
- Multiple arm chains radiating from a central core
- Multivinyls are used to connect arm chain ends to the core

Linear polymers
- Linear polymers with pendant vinyl groups
- Achieved by eliminating the consumption of pendant vinyls via use of asymmetric divinyls or metal–organic frameworks

Branched polymers
- Dendritic polymers with linear chains branched out by multivinyl units
- Achieved by delaying the macroscopic gelation via the "Strathclyde route" etc.

Sequence-controlled polymers
- Linear polymers with specific sequence: ABAB or ABAABA
- Achieved by cyclopolymerization of multivinyls with subsequent degradation

Single-chain-cyclized polymers
- Single-chain polymers with multiple cyclic units and self-knotted structures
- Achieved via homopolymerization of multivinyls, with intracyclization being favoured over intercrosslinking

Homopolymerized, hyperbranched polymers
- Dendritic polymers with every repeat unit as a potential branching unit
- Achieved by kinetically controlled homopolymerization of multivinyls

Well-defined network
- Pseudo-crystallized network with well-aligned/well-positioned linear chains and crosslinkers
- Achieved by host-guest copolymerization of divinyls/monovinyls in porous coordination polymers

Intrachain-linkage (loop) counting
- The first direct, precise, and model-free intrachain-loop-quantification technique in a side-chain-crosslinked network
- Achieved by network disassembly spectrometry

Figure 1.1 Timeline of architecturally complex polymers. Source: Gao et al. [8]/Springer Nature.

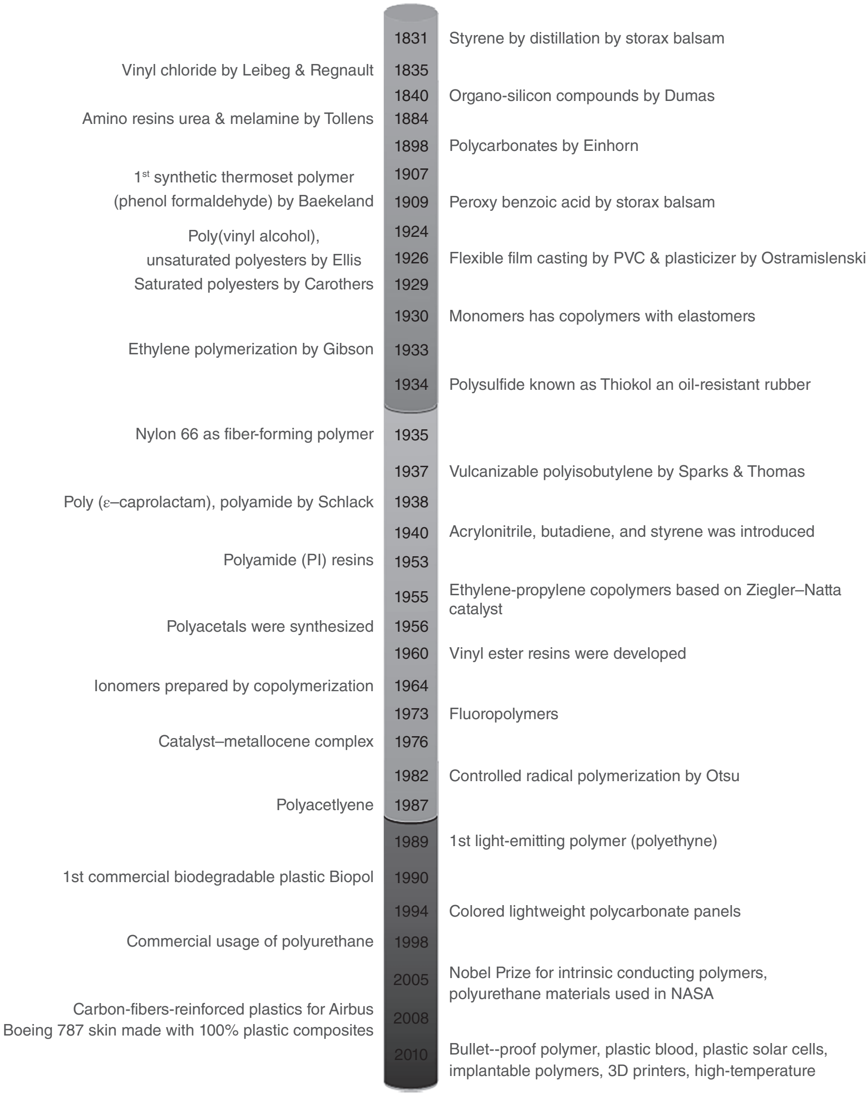


Figure 1.2 History of growth of polymer materials.

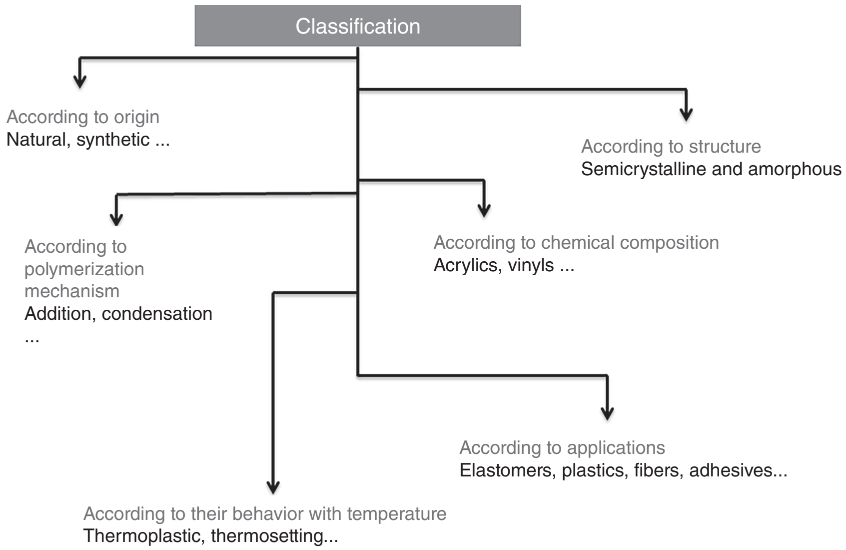
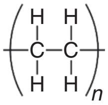
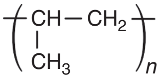
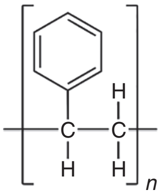
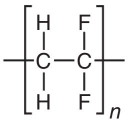
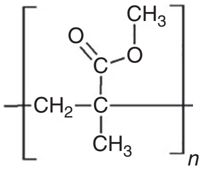
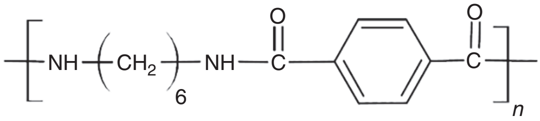


Figure 1.3 Classification of polymers.

material is considered to be the beginning of the truly synthetic plastic era and the plastic industry, although cellulose nitrate (semisynthetic) had been known and in use for some time [7] (Figures 1.1–1.3).

1.1.1 Examples of Polymers

Polyethylene PE: most popular plastic	 $\left(\overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} \right)_n$
Polypropylene PP: used as plastic and as fiber	 $\left(\underset{CH_3}{CH} - CH_2 \right)_n$
Polystyrene PS: economic and resistant.Styrofoam™: foam of PS	
Polyvinylidene fluoride PVDF: high electric and fire resistance	 $\left[\overset{H}{\underset{H}{C}} - \overset{F}{\underset{F}{C}} \right]_n$

Polymethyl methacrylate PMMA: transparent plastic substitute for crystal	
Nylon (polyamides): used as fibers	

1.2 Types of Polymers

1.2.1 Based on Applications

Synthetic polymers can be classified into different types of materials:

Elastomers: Materials with very low modulus of elasticity and high extensibility.
Plastics: Polymers in which, when a sufficiently intense force is applied, they irreversibly deform.
Fibers: Present a high modulus of elasticity and low extensibility.
Coatings: Substances, normally liquid, that adheres to the surface of other materials.
Adhesives: Substances that combine a high adhesion and a high cohesion.

Polymer plasticscan be divided into two classes, thermoplastics and thermosetting plastics, depending on how they are structurally and chemically bonded. Thermoplastic polymers comprise the four most important commodity materials, such as PE, PP, polystyrene, and PVC. The term “thermoplastic” indicates that these materials melt on heating and may be processed by a variety of molding and extrusion techniques. Alternately, “thermosetting” polymers cannot be melted or remitted. Thermosetting polymers include alkyds, amino and phenolic resins, epoxies, polyurethanes, and unsaturated polyesters (Figure 1.4).

Elastomers Fibers Plastics

Figure 1.4 Types of synthetic polymers. Source: Stratasys Ltd., U.S. Department of Agriculture (USDA)/Wikimedia commons/Public Domain, Gigira/Shutterstock.

1.2.2 Classification Based on Temperature Effect

1.2.2.1 Thermosetting Polymers

Most polymers can be broadly classified as either thermoplastics or thermosets. The fundamental physical difference between these two is the bonding between molecular chains – thermoplastics have only secondary bonds between chains, while thermosets also have primary bonds between chains. The names are not only associated with the chemical structure of each but their general thermal and processing characteristics as well, since this basic structural difference greatly impacts material properties. Thermosetting polymers chemically decompose when heated, instead of flowing which is due to a crosslinked structure. Thermoplastic polymers can be melted or molded, while thermosetting polymers cannot be melted or molded in the general sense of the term. Thermoplastic and thermosetting polymers are sometimes identified by other names such as “linear” and “crosslinked,” respectively. It should be noted that the term linear here applies to molecular structure and not to mechanical characteristics. The polymer can be a hard and stiff glass-like solid, a soft and flexible elastomeric rubber, or a viscous liquid depending only on working temperature as compared to two reference temperatures identified as the glasstransition temperature (T_g) and the melt temperature (T_m). All thermoplastic materials may exist in one of these three phases upon changes in the working temperature, while thermosetting polymers generally exist only in the first two phases [9]. The T_g and T_m for different polymers range from well below to well above ambient, and therefore a particular polymer may be glassy, elastomeric, or liquid at room temperature depending only on its chemical composition.

1.2.2.2 Thermoplastic Polymers

Thermoplastic polymers may be either amorphous or crystalline. Crystallinity is important to point out the degree of crystallinity by standards for crystalline metals, ceramics, and other materials [10]. That is, polymers are rarely over 50% crystalline. Crystalline polymers are often more dense than amorphous polymers due to the closer packing of their long-chain molecules and, in general, the following properties are enhanced: hardness, friction and wear, less creep or time-dependent behavior, corrosion resistance, and/or resistance to environmental stress cracking.

1.3 Properties of Polymers

A polymer is an organic material and the backbone of every organic material is a chain of carbon atoms. The carbon atom has four electrons in the outer shell. Each of these valence electrons can form a covalent bond to another carbon atom or a foreign atom. The key to the polymer structure is that two-carbon atom scan has up to three common bonds and still bond with other atoms. The elements found most frequently in polymers and their valence numbers are H, F, Cl, Br, and I with one-valence electron, O and S with two-valence electrons, N with three-valence electrons, and C and Si with four-valence electrons [11].

The ability for molecules to form long chains is vital to producing polymers. Consider the material polyethylene, which is made from ethane gas, C_2H_6. Ethane gas has two carbon atoms in the chain, and each of the two carbon atoms shares two valence electrons with the other. If two molecules of ethane are brought together, one of the carbon bonds in each molecule can be broken and the two molecules can be joined with carbon to carbon bond. After the two mersare joined, there are still two free valence electrons at each end of the chain for joining other mers or polymer chains [12]. The process can continue linking more mers and polymers together until it is stopped by the addition of another chemical that fills the available bond at each end of the molecule. This is called a linear polymer and is a building block for thermoplastic polymers.

1.3.1 Molecular Weight

Macromolecular molecular weight:

$$M_n = M_o X_n$$

where

M_n = number-average molecular weight
M_o = monomer molecular weight
X_n = degree of polymerization (average number of monomer units in a chain).

Mean molecular weight–definition of the various molecular weights

$$M_n = \sum M_i x_i$$

$$M_w = \sum M_i w_i$$

where

M_n = number-average molecular weight
M_w = weight-average molecular weight
M_i = mean molecular weight in size range i
x_i = fraction in number of molecules in range i
w_i = fraction in weight of molecules in range i.

1.3.2 Structural Aspects

The polymer chain is often shown in two dimensions, but it should be noted that it has a three-dimensional structure. Each bond is at 109° to the next and, therefore, the carbon backbone extends through space like a twisted chain of Tinker Toys. When stress is applied, these chains stretch and the elongation of polymers can be thousands of times greater than it is in crystalline structures. The length of the polymer chain is very important. As the number of carbon atoms in the chain is increased to beyond several hundred, the material will pass through the liquid state and become a waxy solid. When the number of carbon atoms in the chain is over a thousand, the solid material PE, with its characteristics of strength, flexibility, and toughness, is obtained. The state change occurs because as the length of the molecules increases, the total binding forces between molecules also increase. It should also be noted that the molecules are not generally straight but are a tangled mass. Thermoplastic materials, such as PE, can be pictured as a mass of intertwined worms randomly thrown into a pail. The binding forces are the result of van der Waals forces between molecules and mechanical entanglement between the chains. When thermoplastics are heated, there is more molecular movement and the bonds between molecules can be easily broken. This is why thermoplastic materials can be remelted. There is another group of polymers in which a single large network instead of many molecules is formed during polymerization. Since polymerization is initially accomplished by heating the raw materials and bringing them together, this group is called thermosetting polymers or plastics. For this type of network structure to form, the mers must have more than two places for bonding to occur; otherwise, only a linear structure is possible. These chains form jointed structures and rings and may fold back and forth to take on a partially crystalline structure. Since these materials essentially comprise one giant molecule, there is no movement between molecules once the mass has been set. Thermosetting polymers are more rigid and generally have higher strength than thermoplastic polymers. Also, since there is no opportunity for motion between molecules in a thermosetting polymer, they will not become plastic when heated (Figure 1.5).

The physical properties of a polymer depend not only on the type of monomers that make up the polymer but also on the stereochemical arrangements of the atoms. In a linear asymmetric polymer chain, the pendant groups can either be arranged into orderly configurations or they can be completely random. The steric order is called tacticity. If all chiral centers have the same configuration, the arrangement of the side groups is called *isotactic*, and if every other chiral center has the same

Figure 1.5 Representation of different molecular structures of the polymer.

Table 1.1 Melting and glass transition temperatures for some of the more common polymeric materials.

Polymer	T_g (atactic)	T_g (isotactic)	T_g (syndiotactic)
Poly(methyl acrylate)	281	272	299
Poly(ethyl acrylate)	249	253	263
Poly(methyl methacrylate)	378	319	433
Poly(n-butyl methacrylate)	293	249	361
Poly(isopropyl acrylate)	267	264	285
Poly(methyl α-chloroacrylate)	416	353	452
Poly(isopropyl α-chloroacrylate)	363	321	392

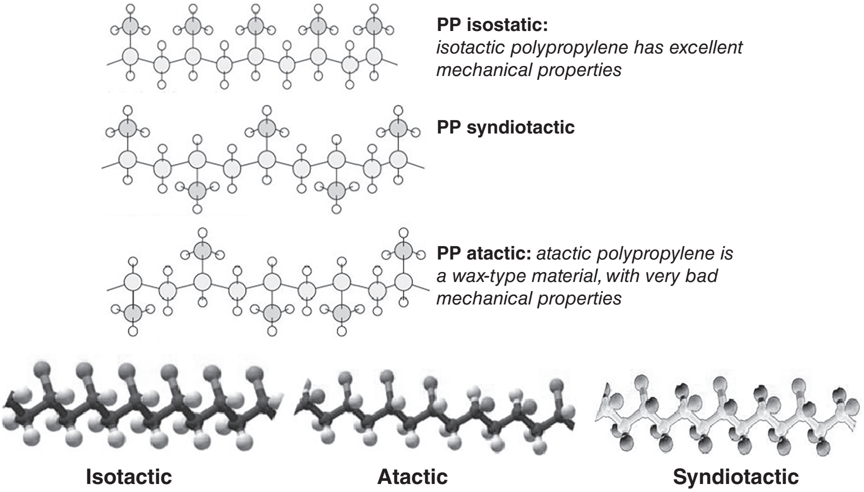


Figure 1.6 Different types of arrangements in polymeric chains.

arrangement, it is called *syndiotactic*, whereas a random arrangement of the side groups is called *atactic* or *heterotactic* (Table 1.1 and Figure 1.6).

An example of tacticity is PP.

1.3.3 Copolymers in Sequence

A copolymer is a polymer that is made up of two or more monomer species. Many commercially important polymers are copolymers, e.g. polyethylene-vinyl acetate (PEVA), nitrile rubber, and acrylonitrile butadiene styrene (ABS). The process in which a copolymer is formed from multiple species of monomers is known as copolymerization [13]. It is often used to improve or modify certain properties of plastics (Figure 1.7).

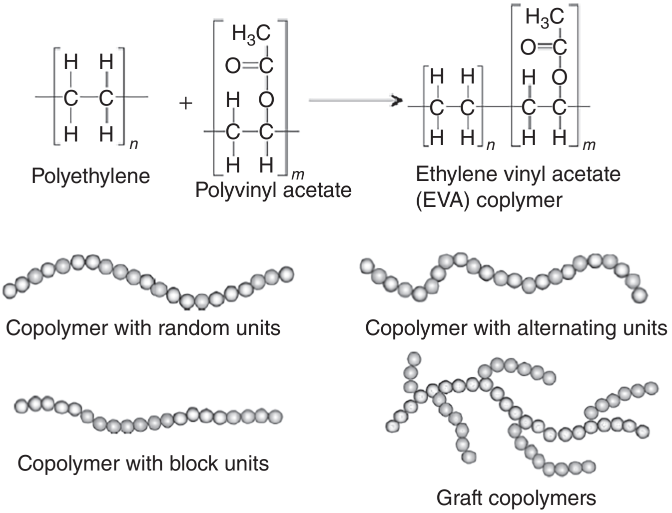


Figure 1.7 Types of copolymer sequences.

1.3.4 Crystallinity of Polymers

1.3.4.1 Solid-State Crystallinity

Crystallinity defines the degree of long-range order in a material and strongly affects its properties. The more crystalline the polymer, the more regularly aligned its chains. Increasing the degree of crystallinity increases hardness and density which is illustrated in poly(ethene). High-density polyethylene (HDPE) is composed of linear chains with little branching. Molecules pack closely together, leading to a high degree of order. This makes it stiff and dense, and it is used for milk bottles and drainpipes. The numerous short branches in low-density polyethylene (LDPE) interfere with the close packing of molecules, so they cannot form an ordered structure. The lower density and stiffness make it suitable for use in films such as plastic carrier bags and food wrapping. Often, polymers are semicrystalline, existing somewhere on a scale between amorphous and crystalline [14]. This usually consists of small crystalline regions (crystallites) surrounded by regions of an amorphous polymer.

1.3.4.2 Factors Favoring Crystallinity

In general, factors causing polymers to be more ordered and regular tend to lead to a higher degree of crystallinity:

a. *Fewer short branches*: allowing molecules to pack closely together
b. *Higher degree of stereoregularity*: syndiotactic and isotactic polymers are more ordered than atactic polymers
c. *More regular copolymer configuration*: having the same effect as stereoregularity [15].

1.3.5 Morphology of the Polymeric Crystals

Morphology refers here to the size and shape of crystals and crystal aggregates. For example, PE is the model semicrystalline polymer. The polymerization methods available during the decades have made it possible to make PE of different crystallinity and morphologies. The high-pressure process first developed in the 1930s yielded branched PE with ~50% crystallinity. Low-pressure processes, developed in the 1950s utilizing metal–organic chemistry, yielded linear PE (~75% crystallinity). Low- and medium-density PE was made by the low-pressure technique replacing part of the ethylene with higher 1-alkenes. The metallocene technology was put into commercial use in the 1990s, and it provides PE with a narrow molar mass distribution and a uniform distribution of comonomer units [16]. The recent availability of monodisperse *n*-alkanes with several hundred carbon atoms using a preparation method has provided new insight into several important aspects of PE morphology. PE is used in large quantities and for many different applications. The properties of PE are controlled by morphology (Figures 1.8 and 1.9).

Figure 1.8 Polymeric monocrystals.

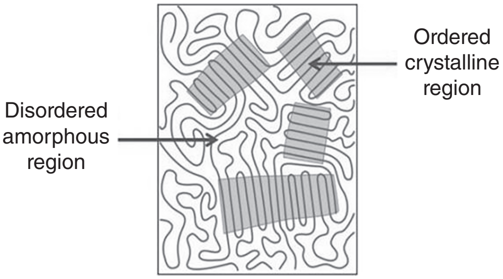
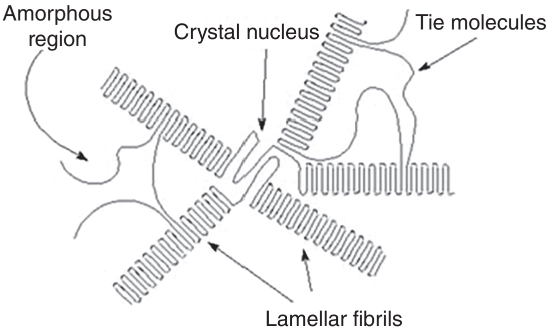


Figure 1.9 Polymer crystalline spherulite.

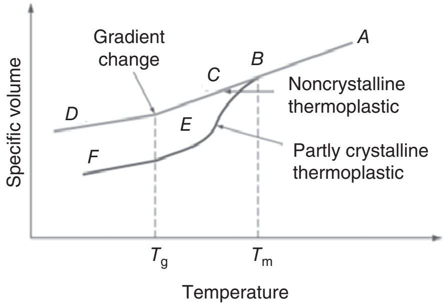


1.3.5.1 Solid-State Thermal Transitions

Crystalline solid–solid transitions are often observed in single-component systems. By changing temperature (or pressure), a crystalline solid can be transformed into another crystalline solid without entering an isotropic liquid phase. These transitions result in material polymorphs. In most cases, crystalline solid–solid transitions are first-order transitions that undergo discontinuous changes in volume, *enthalpy*, and entropy due to crystal packing changes. The magnitude of these changes is usually small compared to the changes occurring from crystalline solid–liquid transitions. Although this transition requires symmetry breaking in structure to qualify as a first-order transition, the positional changes of the molecules to transform from one structure to the next must occur cooperatively, and the displacements cannot be too large [17] (Figures 1.10–1.12).

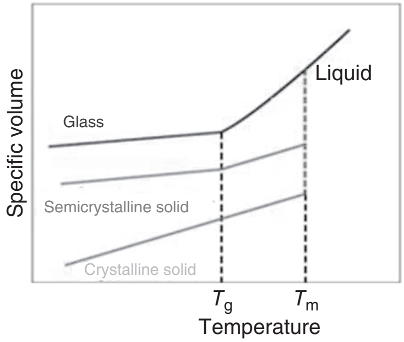
1.3.6 Mechanical Behavior

Polymers exhibit a wide range of stress–strain behaviors as shown in Figure 1.13. The brittle polymer elastically deforms and fractures before deforming plastically. The 100% amorphous curve is a plastic polymer and is similar to curves for many metals. Its behavior begins in the linear elastic deformation region. As the curve transitions from the elastic to plastic deformation typically there is peak stress. For polymer materials, this peak stress is identified as yield stress. As the material is



A = liquid; *B* = liquid of high viscosity
C = undercooled liquid (rubbery)
D = glassy solid;
E = solid crystalline regions in matrix of supercooled liquid
F = solid crystalline regions in glassy matrix
T_g = glass transition temperature
T_m = melting temperature
ABCD = noncrystalline thermoplastics cool throughout the line
ABEF = partially crystalline thermoplastics cool throughout the line

Figure 1.10 Cooling curves for thermoplastic polymers. Source: Rosler et al. [18], John Wiley and Sons, Inc.



T_m: melting temperature → crystalline regions
T_g: glass transition temperature → amorphous regions
Glass transition → changes in the specific heat and the dilatation coefficient

Figure 1.11 Specific volume vs. temperature upon cooling from the liquid melt for polymers with a different structure. Source: Rosler et al. [18], John Wiley and Sons, Inc.

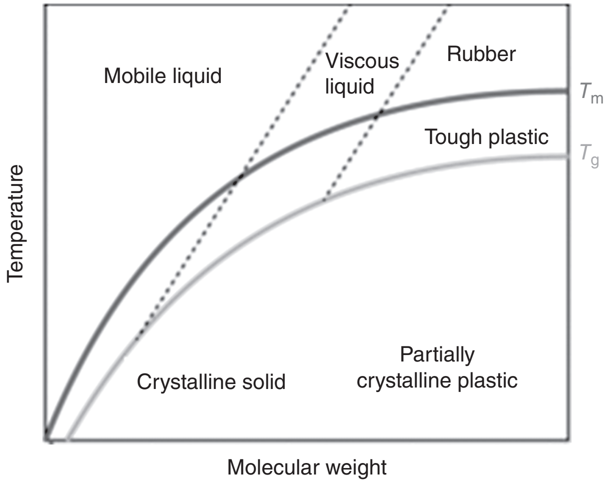


Figure 1.12 Influence of molecular weight. Source: Reprinted with permission from Rosler et al. [18].

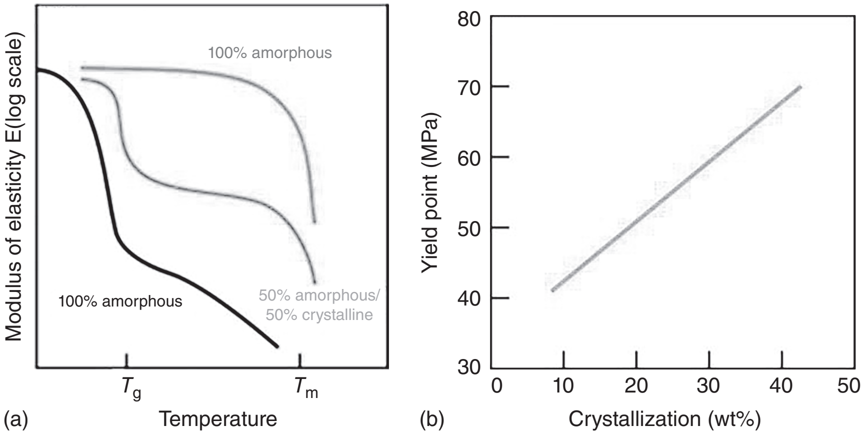


Figure 1.13 (a) Mechanical behaviors of thermoplastics: amorphous, crystalline, and 50/50 amorphous/crystalline, (b) effect of the crystallinity in the modulus of elasticity.

pulled further, fracture occurs. The stress value when the fracture occurs is defined as the tensile strength for polymer materials. The tensile strength can be greater than, equal to, or less than the yield strength. These materials exhibit rubber-like elasticity and will return to their original shape and form unless they are extended to the point of fracture [19].

1.3.7 Polymer Rheology and Processing

Measurements of the rheological properties offer a fast and reliable way to determine molecular weight distribution and long-chain branching, which in combination with the processing conditions, have a decisive influence on the end use product properties [18]. Shear viscosity, elongation viscosity, normal stress differences, stress relaxation, and some other measures and rheological phenomena, of relevance to polymer processing, are discussed in this section. The most widely used polymer processing technologies are extrusion and injection molding.

Polymer processing consists of melting or dissolving a polymeric material, shaping, and solidifying. The choice of whether a melt or solution technique is used depends on (i) chemical stability and (ii) the ability to melt or dissolve [20]. For example, PE is generally melt-processed, since it is stable in the melt but only soluble with some difficulty. Polyacrylonitrile and its copolymers, in composition, are soluble but infusible, so that they are always processed in solution.

1.3.7.1 Polymer Processing Techniques

The following polymer processing techniques are generally employed: (i) Mixing (Polymer additives, Mixing mechanics, Mixing devices), (ii) Extrusion (Extrusion process, Single-screw extruder, Single-screw extruder, Extrusion dies), (iii) Molding (Injection molding, Compression molding, Blow molding, Rotational molding), (iv) Calendering (Process, Arrangements of rolls), and (v) Coating (Fluid-coating process) [21].

The term rheology was first coined by Professor Eugene Bingham of Lafayette College, Indiana, in the 1920s, which originates from the Greek word "rheos" meaning everything flows upon time interval. Thus, rheologyis defined as the science of studying the flow and deformation of matter induced by applied shear forces. From the scope of rheology, all forms of shear behaviors, including the flow of ideal viscous liquids and the deformation of classical elastic solids, can be described by their response to external stresses [22]. These rheological characteristics are highly dependent on the deformation process concerning time. Polymer rheology in the liquid state aims at understanding the complex flow behavior of these materials to model and optimize processing operations. The complexity of the materials also couples with that of the *processing flow* conditions. It suffices to recall that the most used machinery is the extruder where polymers follow helicoidal trajectories before being pumped into a dye and then shaped in many different ways. Rheological studies reduce the flow complexity to a set of basic simple flows because complex flows can be considered as a combination of simpler ones.

The melt rheological properties of filled polymers are sensitive to the structure, concentration, particle size, shape, and surface characteristics of the fillers; rheology offers original means to assess the state of the dispersion in nanocomposites and to investigate the influence of flow conditions upon nanofiller dispersion itself [23].

A better understanding of the rheological properties of polymers is very important for determining the preferred industrial-scale processing conditions, as well as for achieving the desirable physical/mechanical properties in the finished products [24]. Rheometry is the measuring equipment used to assess these rheological properties [25]. This section gives a general idea of current measuring systems: (i) capillary rheometer, (ii) couette (concentric cylinder) rheometer, and (iii) cone-and-plate rheometer.

1.3.7.2 Rheology of Nanocomposites

Rheology is the deformation and material flow study. It is dedicated to the study of viscoelastic materials that include both liquid and solid properties. The rheological behavior of the reinforced polymers depends on many parameters, such as the nature of the fillers (size and shape), the concentration, and the interactions between the fillers and between the polymer and the fillers. These parameters cause not only an increase in viscosity but also particular phenomena such as the existence of a flow threshold, a thixotropic, shearing thinning, or shearing thickening behavior. In the case of nanocomposites, all the rheological characteristics of the conventional filled polymers are generally observed. However, because the size of the charges is extremely small, the surface developed with the polymer matrix is therefore very large [26]. To obtain a reproducible measurement, independent of a human factor such as the altitude of the flow cut, the gradient (of shear, stress, or strain) applied to the fluid must be known. For this, appropriate equipment must be used.

To characterize the rheological properties, various devices allow the polymer viscosity measurements. These devices are called kinematic viscometers or rheometers [27]. For the viscosity measurement, the "two-plate" model is used. It defines the space in which mechanical stress will be applied to the fluid. In this model, the soft material is trapped between two surfaces: one is fixed and the other is mobile, and moves at a constant speed. A shearing motion is then applied to the material to study its ability to flow [28].

1.3.7.3 Theory and Modeling of Nanocomposites Rheology

There are several rheological mathematical models applied to rheograms to transform them into information on fluid rheological behavior [29]. For non-Newtonian fluids, the twomost applied models are the Herschel–Bulkley model and the Bingham model.

1.3.8 Polymer Viscoelasticity

One important characteristic of polymeric materials is their viscoelastic behavior. This means that polymer is elastic because, after a strain due to the application of stress, it is capable of recovering. On the other hand, polymers are viscous because of their capability to creep after the strain.

As shown in Figure 1.14, the creep can be nonlinear, where the strain changes in a nonlinear fashion with time. Upon the release of the stress, the polymer can recover some, but usually undergoes some amount of permanent deformation.

Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. A viscous material exhibits time-dependent behavior when stress is applied while under constant stress and deforms at a constant rate, and when the load is removed, the material has “forgotten” its original configuration, remaining in the deformed state [30]. On the other hand, an elastic material deforms instantaneously when stretched and remembers its original configuration, returning instantaneously to its original state once the stress is removed. Viscoelastic materials have elements of both of these properties and, as such, exhibit time-dependent strain showing a “fading memory.” Such behavior may be linear (stress and strain are proportional) or nonlinear. Whereas elasticity is usually the result of bond stretching along with crystallographic planes in an ordered solid, viscoelasticity is the result of the diffusion of atoms or molecules inside an amorphous material.

The simplest models for the deformation behavior of an ideal material are those of Hookean linear elasticity in the solidstate and Newtonian linear viscosity in the liquid state. The endpoint of elastic deformation is either fracture or plastic flow, with

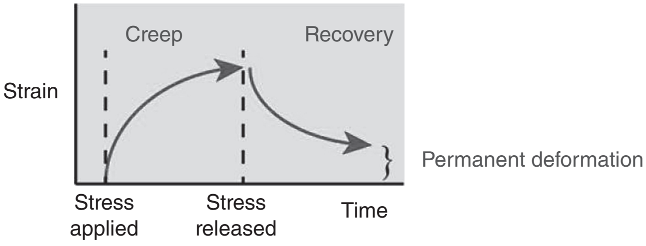


Figure 1.14 Representation of creep and recovery in viscoelastic material.

the latter taking place at constant yield stress in the ideal case. While the behavior of many real materials does approximate to these idealized models that of polymers deviates markedly from them. In particular, their solid-state deformation is time-dependent and nonlinear and so resembles some combination of elastic and viscous responses, at the same time as their melt rheology is also significantly nonlinear [31].

Polymers are characterized by the fact that their behavior under load or deformation is, to a large extent, time-dependent even at room temperature. Moreover, their response to a load or deformation will depend, in some cases, upon any previous load, deformation, or temperature history. This time dependence manifests itself in several forms: two of these are creeping, that is to say, a progressive increase in deformation under a constant load, and stress relaxation, a gradual decrease in stress under a constant deformation. Both these phenomena influence and, in many cases, limit the application of plastics for structural and load-bearing applications.

The contribution of viscous deformation was shown to result in time-dependent permanent deformation (*creep*) under instantaneous, constant stress. Similarly, under an instantaneous constant deformation or strain, viscous deformation can cause *stress relaxation*. Nearly all synthetic and natural polymers used as biomaterials, as well as biological tissues, exhibit viscoelasticity to varying degrees. Noncrystalline or semicrystalline polymers and glasses exhibit free volume and a *glass transition temperature* (T_g) due to the inability of relatively large molecules to organize into a perfectly crystalline network. Below T_g, molecular motions are restricted by time, and the material exhibits glassy or brittle elastic behavior. Near T_g, or more precisely within a temperature range surrounding T_g, the free volume allows some viscous molecular rearrangement, and the material exhibits a viscoelastic response, which becomes increasingly elastomeric (nonlinear elastic) with the increased temperature above T_g. Near the melting temperature, elastic deformation is lost and the material exhibits only viscous flow. Additional background on structure–property relationships including the effects of molecular weight, crystallinity, and crosslinking for noncrystalline and semicrystalline materials (polymers and glasses) is reported. Hydrated biological tissues can also exhibit viscoelasticity due to the permeability of the tissue to fluid flow (poroelasticity) [32].

A stress relaxation test is a simple means of investigating the viscoelasticity of a polymer. To perform this test, a fixed tensile or compressive strain is applied to a sample, and the stress, which decays over time, is monitored [33, 34]. The decrease in stress at a constant strain corresponds to a decrease in the apparent modulus of the polymer. The modulus of a viscoelastic material during a stress relaxation test is often modeled using Eq. (1.1):

$$E(t) = E_\infty + (E_0 - E_\infty)\exp(-t/\tau) \tag{1.1}$$

where (E_0) and (E_∞) are the instantaneous and long-term elastic modulus of the material, respectively, t is time, and τ is the relaxation time constant. As discussed previously, the uncertainty in the literature concerns the origin of changes in the time constant commonly observed when fibers are added to a polymer. In an isotropic solid, the shear modulus (G) and elastic modulus (E) are related by

Poisson's ratio (ν) as shown in Eq. (1.2). For an isotropic, viscoelastic material, at each point in time, the same relationship should hold, as shown in Eq. (1.3). Poisson's ratio is usually considered to be constant in this treatment:

$$E = 2G(1 + \nu) \tag{1.2}$$

$$E(t) = 2G(t)(1 + \nu) \tag{1.3}$$

Thus, Eqs. (1.1) and (1.2) can be used to obtain the time dependence of the shear modulus of a viscoelastic material, as shown in Eq. (1.4):

$$2G(t)(1 + \nu) = 2G_\infty(1 + \nu) + 2(1 + \nu)(G_0 - G_\infty)\exp(-t/\tau) \tag{1.4}$$

$$G(t) = G_\infty + (G_0 - G_\infty)\exp(-t/\tau) \tag{1.5}$$

1.4 Physicochemical Properties of Polymers

1.4.1 Polymers are Very Resistant to Chemicals

Consider all the cleaning fluids in your home that are packaged in plastic. Reading the warning labels that describe what happens when the chemical comes in contact with skin or eyes or is ingested will emphasize the need for chemical resistance in the plastic packaging. While solvents easily dissolve some plastics, other plastics provide safe, nonbreakable packages for aggressive solvents.

1.4.2 Polymers are Both Thermal and Electrical Insulators

A walk through your house will reinforce this concept, as you consider all the appliances, cords, electrical outlets, and wiring that are made or covered with polymeric materials. Thermal resistance is evident in the kitchen with pot and panhandles made of polymers, coffee pot handles, the foam core of refrigerators and freezers, insulated cups, coolers, and microwave cookware. The thermal underwear that many skiers wear is made of PP, and the fiberfill in winter jackets is acrylic and polyester [35].

1.4.3 Polymers are Very Light in Weight with Significant Degrees of Strength

Consider the range of applications, from toys to the frame structure of space stations, or from delicate nylon fiber in pantyhose to Kevlar, which is used in bulletproof vests. Some polymers float in water, while others sink. But, compared to the density of stone, concrete, steel, copper, or aluminum, all plastics are lightweight materials.

1.4.4 Polymers are Processed in Various Ways

Extrusion produces thin fibers or heavy pipes or films or food bottles. Injection molding can produce very intricate parts or large car body panels. Plastics can be molded into drums or be mixed with solvents to become adhesives or paints. Elastomers and some plastics stretch and are very flexible. Some plastics are stretched in processing to hold their shape, such as soft drink bottles. Other polymers can be foamed like polystyrene (Styrofoam™), polyurethane, and PE.

1.4.5 Polymers are Materials With a Seemingly Limitless Range of Characteristics and Colors

Polymers have many inherent properties that can be further enhanced by a wide range of additives to broaden their uses and applications. Polymers can be made to mimic cotton, silk, and wool fibers; porcelain and marble; and aluminum and zinc. Polymers can also make possible products that do not readily come from the natural world, such as clear sheets and flexible films.

1.4.6 Polymers are Usually Made of Petroleum, but not Always

Many polymers are made of repeat units derived from natural gas or coal or crude oil. But building block repeat units can sometimes be made from renewable materials such as polylactic acid from corn or cellulosics from cotton linters. Some plastics have always been made from renewable materials, such as cellulose acetate used for screwdriver handles and gift ribbons. When the building blocks can be made more economically from renewable materials than from fossil fuels, either old plastics find new raw materials or new plastics are introduced.

1.4.7 Polymers are Used to Make Items That Have no Alternatives to Other Materials

Polymers can be made into clear, waterproof films. PVC is used to make medical tubing and blood bags that extend the shelf life of blood and blood products. PVC safely delivers flammable oxygen in non-burning flexible tubing, an antithrombogenic material, such as heparin, can be incorporated into flexible PVC catheters for open-heart surgery, dialysis, and blood collection. Many medical devices rely on polymers to permit effective functioning [36].

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