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Polymer

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Content

Polymers, macromolecules, high polymers, and giant molecules are high-molecular-weight materials composed of repeating subunits. These materials may be organic, inorganic, or organometallic, and synthetic or natural in origin. Polymers are essential materials for almost every industry as adhesives, building materials, paper, cloths, fibers, coatings, plastics, ceramics, concretes, liquid crystals, photoresists, and coatings. They are also major components in soils and plant

and animal life. They are important in nutrition, engineering, biology, medicine, computers, space exploration, health, and the environment. *See also:* **Ceramics (/content/ceramics/121000)**; **Manufactured fiber (/content/manufactured-fiber/404050)**; **Natural fiber (/content/natural-fiber/444700)**

Natural inorganic polymers include diamonds, graphite, sand, asbestos, agates, chert, feldspars, mica, quartz, and talc. Natural organic polymers include polysaccharides (or polycarbohydrates) such as starch and cellulose, nucleic acids, and proteins. Synthetic inorganic polymers include boron nitride, concrete, many high-temperature superconductors, and a number of glasses. Siloxanes or polysiloxanes represent synthetic organometallic polymers. *See also:* **Silicone resins (/content/silicone-resins/623300)**

Synthetic polymers offer a savings in energy requirements over other materials such as metals. Their lightness reduces the consumption of fuel in vehicles and aircraft, and they outperform most metals when measured on a strength-per-weight basis. As properties have improved, polymers have been developed which can be readily and economically fabricated, and which can be used for engineering purposes such as gears, bearings, and structural members.

History

Most of the early discoveries in polymer science were empirical, with polymer chemists often converting naturally occurring materials into materials with enhanced properties. Charles Goodyear (1839) transformed natural rubber (from the rubber tree *Hevea brasiliensis*) to a less heat-sensitive product using sulfur as a crosslinking agent, thus producing an elastic material with greater thermal stability. Alexander Parkes and John W. Hyatt (about 1868) added agents to natural materials such as cellulose and cellulose-derived materials to make them more flexible. Leo H. Baekeland (1907) produced crosslinked polymeric materials from formaldehyde and phenol, called Bakelite. *See also:* **Cellulose (/content/cellulose/118200)**; **Phenolic resin (/content/phenolic-resin/506700)**; **Rubber (/content/rubber/594800)**

In the 1920s, Hermann Staudinger demonstrated that natural and synthetic polymers are not aggregates such as colloids, or cyclic compounds such as cyclohexane, but are long chainlike molecules with specific terminal groups. His work, for which he was awarded the Nobel Prize in Chemistry (1953), is considered the basis for modern polymer science.

In 1928, Herman Mark and Kurt Meyer used x-ray techniques to determine the crystallographic structures of cellulose and natural rubber. The following year, Wallace H. Carothers synthesized and characterized linear (aliphatic) polymers. Shortly thereafter, his group at DuPont synthesized nylon, a fiberforming polyamide. Carothers also coined many of the terms used in polymer science. *See also:* **Polyamide resins (/content/polyamide-resins/533800)**

Nomenclature

Since much of polymer science was developed in industry and within a wide range of disciplines, many polymers have both a common name and a structure-based name specified by the International Union of Pure and Applied Chemistry (IUPAC). Many polymers are commonly known by their acronyms. *See also:* **Organic nomenclature (/content/organic-nomenclature/475250)**

For example, polystyrene or PS is named poly(1-phenylethylene) by the IUPAC, while poly(methyl methacrylate) or PMMA is named poly[(1-metho-xycarbonyl)-1-methylethylene]. *See also:* **Polyacrylate resin (/content/polyacrylate-resin/533500)**; **Polystyrene resin (/content/polystyrene-resin/536900)**

Many companies use trade names to identify the specific polymeric products they manufacture. For example, Fortrel® polyester is a poly(ethylene terephthalate) or PET fiber. Many polymers are generically named, such as rayon, polyester, and nylon. *See also:* **Polyester resins (/content/polyester-resins/534200)**

Composition

Generally, polymers have structures that can be represented by similar or identical repeat units. The repeat units are derived from smaller molecules, called monomers, which react to form the polymer. For example, propylene monomer (structure **1**) and the repeat unit (**2**) it forms in polypropylene are shown below.

$$CH_2\!=\!CH\atop |\atop CH_3 \quad \longrightarrow \quad \left[\!\!\begin{array}{c} CH_2\!-\!CH \\ | \\ CH_3 \end{array}\!\!\right]_n$$

Monomer (1)   Polymer repeat unit (2)
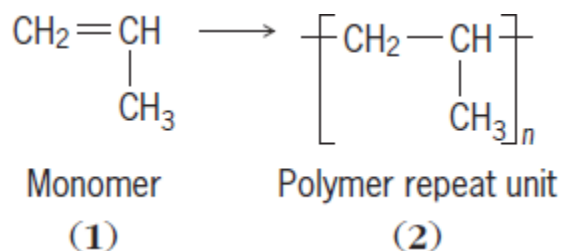
With the exception of its end groups, polypropylene is composed entirely of this repeat unit. The number of units (*n*) in a polymer chain is called the degree of polymerization or DP. *See also:* **Polyvinyl resins (/content/polyvinyl-resins/537500)**

Other polymers, such as proteins, can be described in terms of the approximate repeat unit (**3**)

$$\left[\!\!\begin{array}{c} O \\ \| \\ NH\!-\!C\!-\!CH \\ | \\ R \end{array}\!\!\right]_n$$

(3)
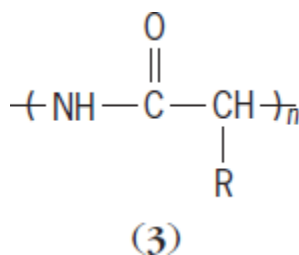
where the nature of R (a substituted atom or group of atoms) varies. *See also:* **Protein (/content/protein/550200)**

Primary structure

The sequence of repeat units within a polymer is called its primary structure. Unsymmetrical reactants, such as substituted vinyl monomers (**4**),

$$\begin{array}{ccc} H & & H \\ \diagdown & & \diagup \\ & C\!=\!C & \longrightarrow \\ \diagup & & \diagdown \\ H & & R \end{array}$$

Vinyl monomer (4)
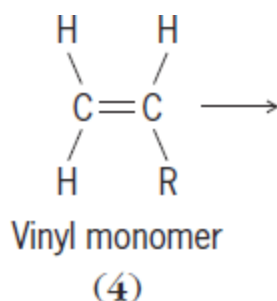
react almost exclusively to give a "head-to-tail" product (**5**), in which the R substituents occur on alternate carbon atoms. A variety of head-to-head structures (**6**)

Head-to-tail

(5)

Head-to-head/tail-to-tail

(6)
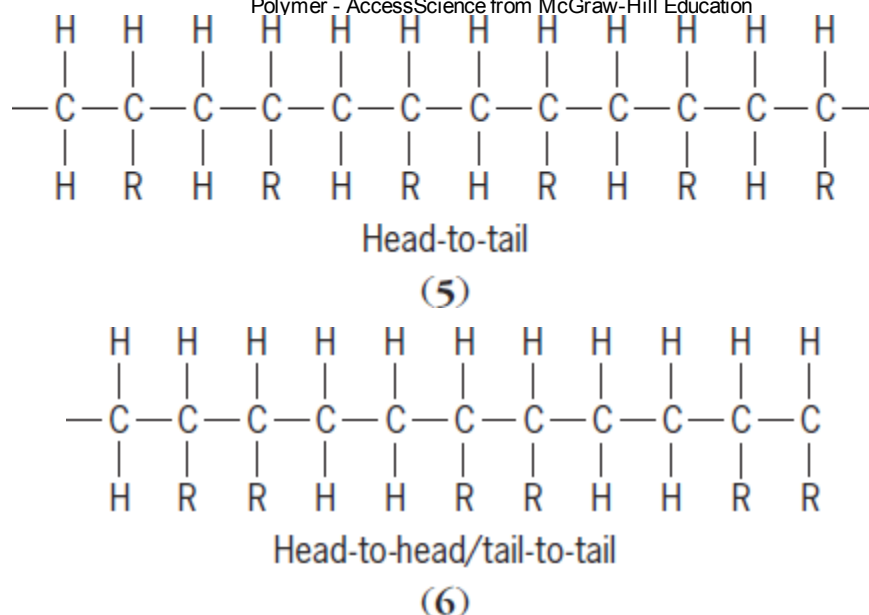
are also possible. Each R-substituted carbon atom is a chiral center (one atom in a molecule attached to four different groups) with different geometries possible. Arrangements where the substituents on the chiral carbon are random are referred to as atactic structures. Arrangements where the geometry about the chiral carbon alternates are said to be syndiotactic. Structures where the geometry about the chiral atom have the same geometry are said to be isotactic. Both syndiotactic and isotactic polymers are stereoregular. *See also:* **Polymer stereochemistry and properties (/content/polymer-stereochemistry-and-properties/802700)**

Stereoregular polymers are produced using special stereoregulating catalyst systems. A series of soluble catalysts have been developed that yield products with high stereoregularity and low chain size disparity. As expected, polymers with regular structures—that is, isotactic and syndiotactic structures—tend to be more crystalline and stronger.

Polymers can be linear or branched with varying amounts and lengths of branching (**Fig. 1**). Most polymers contain some branching.
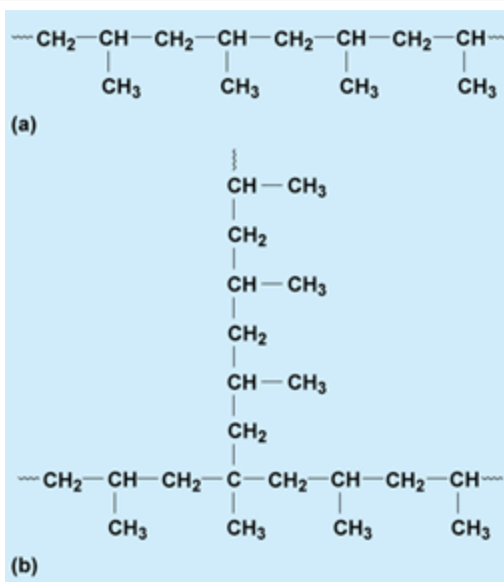
Fig. 1 Polymer structures: (*a*) linear, (*b*) branched.

Copolymers are derived from two different monomers, which may be represented as A and B. There exists a large variety of possible structures and, with each structure, specific properties. These varieties include alternating, random, block, and graft (**Fig. 2**). *See also:* **Copolymer (/content/copolymer/160850)**
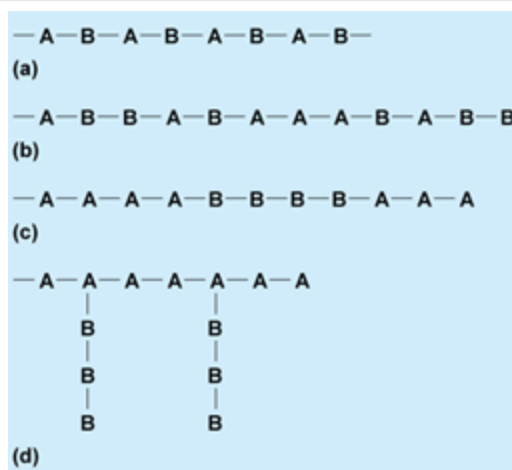
Fig. 2 Copolymer structures: (*a*) alternating, (*b*) random, (*c*) block, (*d*) graft.

Secondary structure

Secondary structure refers to the localized shape of the polymer, which is often the consequence of hydrogen bonding and other hydrophilic and hydrophobic interactions. (Nonpolar regions tend to clump with other nonpolar regions, while polar regions tend to clump with other polar regions.) Most flexible to semiflexible linear polymer chains tend toward two structures—helical and pleated sheet/skirtlike. The pleated skirt arrangement is most prevalent for polar materials where hydrogen bonding can occur. In nature, protein tissue is often of a pleated skirt arrangement. For both polar and nonpolar polymer chains, there is a tendency toward helical formation with the inner core having "like" secondary bonding forces. *See also:* **Hydrogen bond (/content/hydrogen-bond/328800)**

Tertiary structure

Tertiary structure refers to the overall shape of a polymer, such as in polypeptide folding. Globular proteins approximate rough spheres because of a complex combination of environmental and molecular constraints, and bonding opportunities. Many natural and synthetic polymers have "superstructures," such as the globular proteins and aggregates of polymer chains, forming bundles and groupings.

Quaternary structure

Quaternary structure refers to the arrangement in space of two or more polymer subunits, often a grouping together of tertiary structures. For example, hemoglobin (quaternary structure) is essentially the combination of four myoglobin (tertiary structure) units. Many crystalline synthetic polymers form spherulites. *See also:* **Hemoglobin (/content/hemoglobin/313800)**

Synthesis

For polymerization to occur, monomers must have at least two reaction points or functional groups. There are two main reaction routes to synthetic polymer formation—addition and condensation. In chain-type kinetics, initiation starts a series of monomer additions that result in the reaction mixture consisting mostly of unreacted monomer and polymer. Vinyl polymers, derived from vinyl monomers and containing only carbon in their backbone, are formed in this way. Examples of vinyl polymers include polystyrene, polyethylene, polybutadiene, polypropylene (**7**),

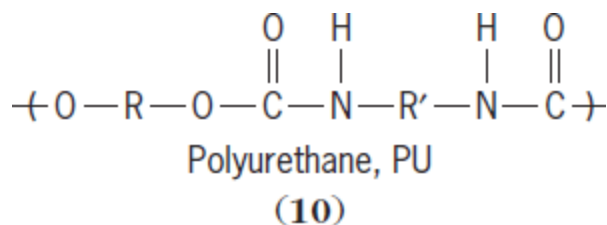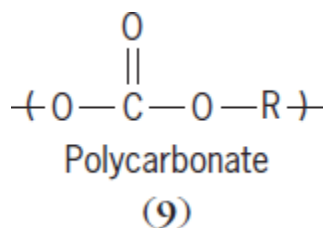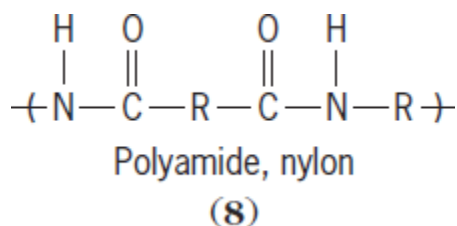$$\left[CH_2CH \atop \underset{\displaystyle CH_3}{|} \right]_n$$

Polypropylene, PP

(**7**)
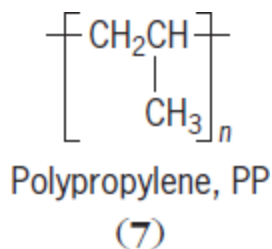
and poly(vinyl chloride). *See also:* **Polymerization (/content/polymerization/535300)**; **Polyolefin resins (/content/polyolefin-resins/535900)**

The second main route is a step-wise polymerization. Polymerization occurs in a step-wise fashion so that the average chain size within the reaction mixture may have an overall degree of polymerization of 2, then 5, then 10, and so on, until the entire mixture contains largely polymer with little or no monomer left. Polymers typically produced using the step-wise process are called condensation polymers, and include polyamides (**8**), polycarbonates (**9**), polyesters, and polyurethanes (**10**).

$$\begin{array}{ccccccc} H & O & & O & H \\ | & \| & & \| & | \\ +N\!-\!C\!-\!R\!-\!C\!-\!N\!-\!R+ \end{array}$$

Polyamide, nylon

(**8**)

$$\begin{array}{c} O \\ \| \\ +O\!-\!C\!-\!O\!-\!R+ \end{array}$$

Polycarbonate

(**9**)

$$\begin{array}{ccccccc} & O & H & & H & O \\ & \| & | & & | & \| \\ +O\!-\!R\!-\!O\!-\!C\!-\!N\!-\!R'\!-\!N\!-\!C+ \end{array}$$

Polyurethane, PU

(**10**)

Condensation polymer chains are characterized as having a noncarbon atom in their backbone. For polyamides the noncarbon is nitrogen (N), while for polycarbonates it is oxygen (O). Condensation polymers are synthesized using melt (the reactants are heated causing them to melt), solution (the reactants are dissolved), and interfacial (the reactants are dissolved in immiscible solvents) techniques. **Table 1** lists some addition and condensation polymers. *See also:* **Polyurethane resins (/content/polyurethane-resins/537400)**

Table 1 - Polymers and amounts synthesized annually in the United States		
Polymer	**Type of synthesis**	**Amount 10^6 lb**

Table 1 - Polymers and amounts synthesized annually in the United States		
Ureas	Condensation	1,900
Phenolics	Condensation	3,300
Polyethylene	Addition	25,000
Polypropylene	Addition	10,000
Polystyrene	Addition	6,000
Poly(vinyl chloride)	Addition	11,000
Polyacrylonitrile	Addition	500
Polyamides, nylons	Condensation	30,000
Olefins	Addition	2,500
Polybutadiene	Addition	1,100
Styrene-butadiene	Addition	2,200

Properties

The properties of polymeric materials are determined by their molecular properties and morphology. Polymer morphology in turn depends on the polymerization conditions.

Molecular properties

These include molecular size and weight, molecular structure or architecture, molecular weight distribution, polarity, and flexibility of the polymeric chains (or chain segments between crosslinks in cured or vulcanized polymers). Molecular properties taken together determine the attractive forces between the molecules, the morphology or arrangement of masses of molecules, and the general behavior of the polymer.

Molecular weight

The molecular weight of a particular polymer chain is the product of the number of units times the molecular weight of the repeating unit. Polymerization reactions, both synthetic and natural, generally produce products with varying chain lengths. [The exception is the biochemical reactions that produce enzymes (proteins) and nucleic acids (such as DNA), which have precise molecular weights and chain orientations critical to their function.]

A polymer's varying chain lengths result in a product with a distribution of molecular weights. This molecular weight distribution may be narrow or broad, monomodal or polymodal, depending on the polymerization conditions.

Two statistical averages describe polymers, the number-average molecular weight $\overline{M}_n$ and the weight-average molecular weight $\overline{M}_w$. The $\overline{M}_n$ is particularly dependent on the number of polymer chains with a specific chain length, while the $\overline{M}_w$ is dependent on the size distribution of the polymer chains. The $\overline{M}_n$ is determined using procedures that are related to the number of chains of a particular length. Colligative properties are dependent on the number of particles present, and can be used to determine $\overline{M}_n$. These techniques include membrane osmometry, vapor-phase osmometry, ebulliometry (boiling-point elevation), cryoscopy (melting-point depression), end-group analysis, and osmodialysis. Light-scattering photometry is the most often used technique for measuring $\overline{M}_w$.

Since polymers generally greatly increase the viscosity (resistance to flow) of solutions containing them, viscometry is often used to determine the relative molecular weight of polymers. Today, combinations of gel permeation chromatography and light-scattering photometry can be used to determine both average molecular weight and the molecular weight of narrow molecular weight groupings. *See also:* **Light-scattering techniques (/content/light-scattering-techniques/381750)**; **Molecular weight (/content/molecular-weight/431100)**; **Scattering of electromagnetic radiation (/content/scattering-of-electromagnetic-radiation/605200)**; **Viscosity (/content/viscosity/733900)**

Size

Size is the most important property of polymers. Size allows storage of information (nucleic acids and proteins) and allows polymeric materials to "remember" when reversible movement occurs; in cases where movement is not reversible, polymer structures are a consequence of past treatment such as bending, stretching, melting—any action that distorts or moves polymer chains or segments). For large chains, entanglement occurs, introducing physical crosslinking and enhancing the ability of the polymers to remember and return to original molecular structures after applied stress/strain. An aspect of this remembering involves the need for segments of a polymer chain to accompany adjacent polymer segments. Thus, for space travel applications, even when the vacuum is enough to allow segmental "evaporation" of external polymer chains, some of the chain remains connected, trapped within the interior of the polymer matrix, preventing total removal. Polymeric materials are used extensively on the space shuttles.
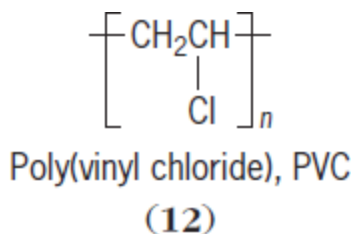
Attractive forces

Size also accounts for an accumulation of the interchain (between molecules) and intrachain (within the same molecule) secondary attractive forces. These secondary forces, called van der Waals forces, are composed of London or dispersion forces, dipole-dipole forces, and hydrogen bonding. For a nonpolar polymer, such as polyethylene (**11**),

$$+ CH_2CH_2 +_{\overline{n}}$$
Polyethylene, PE
(**11**)
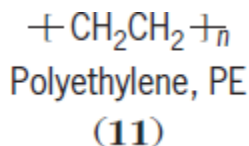
the attractive forces for each unit are about 2 kcal/mole per repeating unit. For a polyethylene chain 1000 units long, the cumulative dispersion attractive forces would be about 2000 kcal/mole, which is well above the carbon-carbon bond strengths so that even low-molecular-weight polymer chains are nonvolatile. As the temperature is increased, polymers will decompose prior to volatilization. *See also:* **Chemical bonding (/content/chemical-bonding/126500)**; **Intermolecular forces (/content/intermolecular-forces/349400)**

For polar polymers, such as poly(vinyl chloride) (**12**),

$$\left[CH_2CH \atop | \atop Cl \right]_n$$
Poly(vinyl chloride), PVC
(**12**)

attractive forces include both dispersion and dipole-dipole forces so that the total attractive forces are proportionally larger than those for polyethylene. Examples of polar polymers include poly(vinyl acetate) (**13**), poly(ethylene glycol) (**14**), and poly(methyl methacrylate) (**15**). For polymers that can take advantage of hydrogen bonding, the attractive forces are even greater. Such polymers include poly(vinyl alcohol), proteins, polysaccharides, nucleic acids, and nylons (**16**).

$$\left[CH_2 - \underset{\underset{OCOCH_3}{|}}{CH} \right]_n$$

Poly(vinyl acetate)

(13)

$$\left[OCH_2CH_2 \right]_n$$
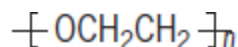
Poly(ethylene glycol), PEG

(14)

$$\left[CH_2 - \underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \right]_n$$

Poly(methyl methacrylate), PMMA

(15)

$$\left[NH - (CH_2)_6 - NH - \overset{\overset{O}{\|}}{C} - (CH_2)_4 - \overset{\overset{O}{\|}}{C} \right]_n$$

Nylon 6,6

(16)

Hydrogen bonding is so strong in cellulose that cellulose is not soluble in water until the inter- and intrachain hydrogen bonds are broken. Thus, "wood shaping" is often accomplished by breaking the hydrogen bonds by addition of sodium hydroxide. After the wood is shaped, the sodium hydroxide is washed away and the hydrogen bonds form again, allowing the wood to retain a new shape. This principle is similar to that of permanent press clothing, where crosslinks are introduced to retain fabric shape.
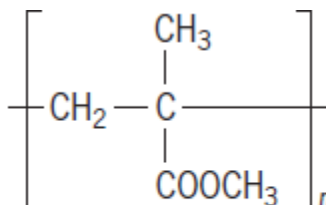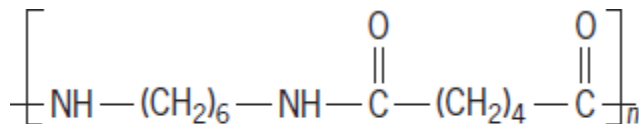
Morphology

As bonding forces and symmetry increase, the tendency to form regular structures increases, and since the inter-and intrachain forces are inversely proportional to the square of the distance, the chains are able to reside closer together. Polymers often have a combination of ordered regions, called crystalline regions, and disordered or amorphous regions. The amorphous regions contribute to polymers' flexibility and diffusivity of gases and other materials. At low temperatures these regions are rigid, but as the temperature increases there is a temperature range where local or segmental chain mobility occurs. This temperature range is called the glass-phase transition temperature, T_g. Polymers are flexible only above their glass-phase transition temperature.

Regions where polymer chains are aligned in an orderly manner are called crystalline regions. Crystalline regions contribute to strength and resistance to external forces, including chemical attack. Crystalline regions can be melted. At the melting point or range, whole-chain movement can occur.

While crystalline regions add strength to a material, such regions are both rigid and brittle. The amorphous regions, where the chains are in a more random orientation, increase flexibility but decrease the strength of a material. Most commercial polymers have a balance between amorphous and crystalline regions, allowing a balance between flexibility and strength.

Crystallization is favored by the presence of regularly spaced symmetrical units. This is reinforced by the presence of regularly spaced polar groups that can form secondary dipole-dipole interactions. Polymers such as polyamides (nylons), polycarbonates (**17**),


Polycarbonate, PC
(**17**)
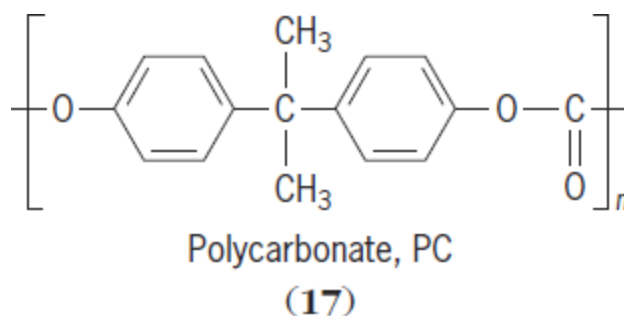
and polyesters tend to form crystalline polymers because of the presence of additional secondary forces. Polymers such as linear polyethylene (with little or no branching) tend to be crystalline because of their symmetry and the ability of their chains to closely approach one another.

Viscoelastic materials

Polymers are viscoelastic materials, meaning they can behave as liquids and solids. When they behave as liquids, their actions can be described by Newton's law, where the applied stress is proportional to the rate of strain. For materials behaving as solids, the mechanical properties can often be described in terms of a spring using Hooke's law, where the applied stress is proportional to the resultant strain. Stress is force per unit area, and strain or elongation is the extension per unit length. *See also:* **Stress and strain (/content/stress-and-strain/660300)**

A reinforced or crystallizable elastomer exhibits a relatively low breaking stress but a high elongation. Ductile polymers, such as polyethylene and polypropylene, "give" or "yield," and at high elongations some strengthening and orientation occur. A brittle polymer, such as polystyrene, does not give much and breaks at a low elongation. A fiber exhibits high strength, high stiffness, and little elongation. In each case, the particular property is dependent on the temperature and the rate in which the stress is applied. Thus, at low temperatures where segmental and whole-chain mobility does not occur, the material can act as a solid. In addition, when a stress is rapidly applied so that chain or segmental mobility is not able to engage, the material will also act as a solid. Thus, a polymer that is brittle or "" at low temperature may become ductile with Newtonian behavior at higher temperatures where segmental or chain mobility can occur (**Fig. 3**). *See also:* **Elasticity (/content/elasticity/215000)**
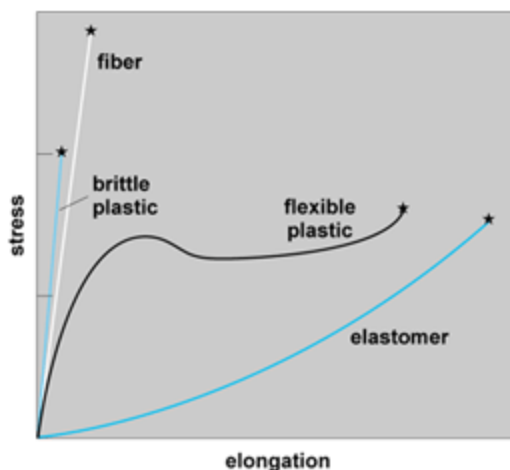
Fig. 3 Stress-elongation behavior of typical classes of polymer (not drawn to scale). The star represents the point at which failure occurs.

When an applied stress is removed, some or all of the deformation may be recovered, with the material returning to its original shape. The term "creep" is used to describe irreversible deformation. The term "elastic memory" is used to describe situations where a polymer is heated and then deformed and then cooled rapidly enough so that the polymer chains are "frozen" in place, with the material retaining the "deformed" shape. *See also:* **Creep (materials) (/content/creep-materials/167300)**

Industrial Polymer Processes

There are about 10,000 American companies active in the general area of synthetic polymers. These companies can be divided into manufacturers, processors, and fabricators. Over 200 companies produce the bulk polymers that are used by the other two groupings of companies. These polymers are generally sent to processor companies as solid pellets in a variety of shapes, including spheres and rice-grain-like. While most manufacturers produce bulk polymers in large quantities, more companies are producing specialty polymers for specific uses.

While some processors make their own polymers, most purchase the raw polymer material from manufacturers. Processors may specialize in a particular product or group of products (such as textiles or tires) or with certain polymers, such as nylons or polyethylenes, or the production of certain forms of material, such as pipes, adhesives, coatings, composites, or sheets. They may also specialize in a particular type of processing, such as blow molding.

The majority of industrial processors are involved in the fabrication and finishing of polymer-containing products. Fabrication includes machining, forming, and fashioning.

The properties of processed polymers are dependent on the conditions of processing such as cooling rate, temperature, duration of application of heat, and pressure. The drawing or pulling of materials as they exit the processing machine can have a profound effect on the properties of a material. Materials with properties that are the same in all directions are called isotropic. Fibers and films that are pulled in one or two directions are stronger in the direction of the applied stress because of the preferential aligning of the polymer chains in the direction of the pull. Thus, fibers are much stronger in the "length" direction because this is the direction of the applied stress.

There are a number of fabrication techniques. In blow molding, air is blown into a hot tube held in a mold for the production of bottles and other hollow shapes.

In extrusion, a hot melt is forced through a hole, or die, with an opening shaped to produce the desired shape. Extrusion and molding techniques are combined to produce sheet foams. Films can also be made using extrusion when air is forced through a tube. Through control of the air pressure, films of varying thicknesses can be made. Films and sheets can also be produced using calendering, where the hot polymer is forced between tightly fitted rollers. These sheets can be formed into various shapes using thermoforming, where the heated sheet is forced against the contours of a mold by a positive pressure or vacuum.

Injection molding can be used to shape thermoplastics. The material is softened and then forced into a relatively cold mold. Pipes, films, rods, and fibers can be made using injection molding.

In casting, fluid materials are poured into molds of the desired shape and then allowed to cool or cure (crosslink). In some sense, painting can be considered to be a casting operation. *See also:* **Plastics processing (/content/plastics-processing/526800)**

Applications

The usefulness of polymers depends on their properties, abundance, availability, and cost, including shipping or transportation, manufacture, fabrication, and environmentally related factors. Polymer properties are related to a variety of factors, including chain size, distribution of chain sizes, resistance to chemical attack, degradation (both biological and physical), flammability, dyeability, comfort, ease of fabrication, weatherability, and strength.

Fibers

Fibers are polymer materials that are strong in one direction, and they are much longer (>100 times) than they are wide. Fibers are usually formed by pulling the fiber in one direction. This orients the polymer chains, giving the fiber preferential strength in the direction of the pull. Fibers formed from symmetrical polymers allow the close approach of the polymer chains, resulting in more effective secondary bonding. The attractive forces between chains need to be relatively high, so polymers that engage in dipole-dipole seconding bonding are preferred. Fibers are to have little or no local mobility so that their use temperature is below the T_g and melting point (T_m). A small amount of crosslinking is generally introduced to lock in a preferred shape. **Table 2** contains selected synthetic fibers.

Table 2 - Industrially important synthetic fibers		
Fiber	**Definition**	**Uses**
Acrylic	85% or more acrylonitrile units	Carpeting, skirts, socks, slacks, sweaters, blankets, draperies
Modacrylic	35–85% acrylonitrile units	Simulated fur, scatter rugs, stuffed toys, paint rollers, carpets, hairpieces
Polyester	85% or greater ester units	Permanent press wear, skirts, shirts, slacks, underwear, blouses, rope, fish nets, tire cord, sails, thread
Nylon	Polyamide	Carpeting, upholstery, tents, blouses, sails, suits, stretch fabrics, tire cord, curtains, rope, nets, parachutes
Polyurethane	85% or more urethane units	Girdles, bras, slacks, bathing suits, pillows
Rayon	Regenerated cellulose, with substituents replacing not more than 15% of the hydrogen's of the hydroxyl groups	Dresses, suits, slacks, tire cord, ties, curtains, blankets, blouses
(Rayon) acetate	More than 92% OH substituted	Dresses, shirts, slacks, cigarette filters, upholstery, draperies
Triacetate	Reaction of cellulose with acetic acid or acetic anhydride	Skirts, dresses, sportswear
Fibrous glass		Composites, insulation
Olefins	Polypropylene, polyethylene	Synthetic grass, rugs

Elastomers

Elastomers (or rubbers) are polymeric materials that can be distorted through the application of force, and when the force is removed, the material returns to its original shape; this characteristic is called memory. Memory is a result of physical or, more normally, chemical crosslinks. The driving force for the return to the original shape is entropy. In the rest state, the polymer chains in the elastomer have a high degree of disorder. As the material is distorted, the polymer chains become

more organized. When the distorting force is released, the elastomer returns to the original disordered state, taking advantage of the increase in disorder or entropy that results when it moves from a situation of greater order to a situation of lesser order. Products with low amounts of crosslinking, such as rubber bands, are more easily deformed or stretched. As the amount of crosslinking increases, the force needed to distort the elastomer increases and the material becomes harder. In order for elastomers to easily stretch, the attractive forces between chains must be low and the material must be above the temperature where local segmental mobility occurs—that is, it must be above the T_g. These properties are found in many hydrocarbon-intense polymers (**Table 3**).

Table 3 - Synthetic elastomers	
Elastomer	**Use**
Acrylonitrile-butadiene-styrene, ABS	Oil hoses, fuel tanks, pipe, appliance and automotive housings
Butadiene rubber, BR	Tire tread, hose, belts
Butyl rubber, IIR	Inner tubes, cable sheathing, roofing, seals, tank liners, coated fabrics
Chloroprene rubber, polychloroprene, CR	Tire and cable insulation, hoses, footwear, mechanical automotive products
Epichlorohydrin (epoxy copolymers)	Seals, gaskets, wire and cable insulation
Ethylene-propylene rubbers, EP, EPDM	Cable insulation, window strips
Fluoroelastomers	Wire and cable insulation, aerospace applications
Ionomers, mostly copolymers of ethylene and acid-containing monomers reacted with metal ions	Golf ball covers, shoe soles, weather stripping
Natural rubber, polyisoprene, NR	Tires, bushings, couplings, seals, footwear, belting
Nitrile rubber (random copolymer of butadiene and acrylonitrile), NBR	Seals, automotive parts that are in contact with oils and gas, footwear, houses
Polysulfide	Adhesives, sealants, hose binders
Polyurethanes	Sealing and joints, printing rollers, tires, footwear, wire and cable covering
Silicons, mostly polydimethylsiloxanes	Medical-application body parts, outer space applications, flexible molds, gaskets, seals
Styrene-butadiene rubber, SBR	Tire tread, footwear, wire and cable covering

Plastics

Plastics are materials that have properties between fibers and elastomers—they are hard and flexible. Polymers that may be fibers or elastomers may also be plastics (**Table 4**). Crystalline nylon is a good fiber, whereas less crystalline nylon is a plastic.

Table 4 - Synthetic elastomers	
Plastic	**Use**
Epoxies	Coatings, laminates, composites, molding, flooring
Urea-formaldehyde resins	Molding compounds, dinnerware
Phenol-formaldehyde resins	Molding compounds
Melamine-formaldehyde resins	Dinnerware, table tops
Polytetrafluoroethylene	Electrical components, nonsticking surfaces, gaskets

Table 4 - Synthetic elastomers	
Polypropylene	Automotive parts, toys, housewares, appliance parts
Polystyrene	Containers, recreational equipment, housewares, appliance parts
Poly(vinyl chloride) and copolymers	Pipes, fittings, sheets, flooring materials, automotive parts
Polycarbonates	Tail light lens, bullet-resistant vests, appliance housings, signs, bottles
Polysulfones	Mechanical parts, small appliances, electrical connectors
Poly(phenylene sulfide)	Electrical and mechanical parts
Polyesters	Apparel, home furnishings
Polyethylenes	Containers, bottles, housewares, pipe and fittings
Styrene-acrylonitriles	Appliance housings, housewares
Poly(methyl methacrylate)	Signs, glazing, lighting, fixtures, automotive lenses, solar panels
Poly(phenylene oxide)	Business machine housings, electrical parts, automotive parts

Coatings and adhesives

Coatings and adhesives are generally derived from polymers that are members of other groupings. For instance, polysiloxanes are elastomers, but also are used as adhesives. Poly(methyl methacrylate) is a plastic and coatings. Coatings or coverings are generally highly viscous (low-flowing) materials. The major use of coatings is for protection. Coatings resist normal wear and tear and degradation due to rain, sunlight, snow, ionizing radiation, and temperature. They protect housing, documents, chairs, stoves, cars, tables, bridges, and so on. Coatings must adhere to the surface to which they are applied. Coatings are generally a mixture of a liquid (vehicle), binder (adhesive), and one or more colorants (pigments). They generally contain a number of additives, which provide added protection against ionizing radiation and mildew, and decreased drying time.

In comparison to coatings that are required to adhere to only one surface, adhesives are used to join two surfaces together. Many good adhesives are also good coating materials. Adhesion for both coatings and adhesives can occur for a number of reasons, including physical interlocking, chemical adhesion where primary bonding occurs between the adhesive and the surfaces being joined, secondary bonding where hydrogen bonding or polar bonding occurs between the adhesive and bonded materials, and resistance to flow (viscosity) where movement is restricted because of the viscous nature of the adhesive material. *See also:* **Adhesive (/content/adhesive/011000)**

Some industrially important adhesives and coatings are the following:

Acrylic acid and acrylic ester polymers	Polysiloxanes
Acrylonitrile-butadiene copolymers	Polyurethane resins
Aromatic polyamides	Poly(vinyl acetate)
Butyl rubber	Poly(vinyl alcohol)
Cellulose and starch derivatives	Poly(vinyl butyral)
Epoxy resins	Poly(vinyl chloride)
Phenol-formaldehyde	Resorcinol-formal-dehyde
Poly(alkyl cyanacrylates)	Styrene-butadiene copolymers
Polyamides	Unsaturated poly-ester resins
Polychloroprene	Urea-formaldehyde
Polyisobutylene	Vinyl acetate-ethyl-ene copolymers
Poly(methyl meth-acrylate)	

Laminates

The combination of an adhesive and adherent is a laminate. Laminates include products that are produced with wood as the adherent and phenolic-formaldehyde, urea-formaldehyde, epoxy, resorcinol-formaldehyde, and polyester resins as the adhesive. The major wood laminate is plywood. Laminates of paper or textile include Formica and Micarta. Laminates are also used as mechanical, electrical, and general-purpose structural materials. *See also:* **Composite laminates (/content/composite-laminates/757513)**

Sealants and caulks

Sealants and caulks provide barriers to gases, liquids, and solids; maintain pressure differences; and moderate thermal and mechanical shock. While adhesives are used for "load transfer" requiring high shear and tensile strengths, sealants act as insulators and shock attenuators and do not require high shear and tensile strengths.

Composites

Composites are materials that contain strong fibers (reinforcement) embedded in a matrix or resin. Composites are found in automobiles, fighter and bomber planes, the "reusable" space shuttle, shafts of golf clubs (graphite), synthetic body parts, and marine craft (fibrous glass). *See also:* **Polymer composite (/content/polymer-composite/535200)**

Films

Films are two-dimensional forms of plastic that are thick enough to be coherent, but thin enough to be easily folded and creased without cracking. Sheeting is a two-dimensional form of plastic that is generally thicker than a film but generally does not easily fold or crease without cracking.

Polyblends

Polyblends are made by mixing polymeric components together. Most are heterogeneous materials in which one polymeric material is embedded in another polymer. The components of polyblends adhere using secondary forces.

Liquid crystals

Liquid crystals (LCs) are materials that undergo physical reorganization where at least one of the rearranged structures involve molecular alignment along a preferred direction, causing the material to exhibit behavior that is directionally dependent. LCs serve as one of the major building blocks of communications industries, including computers and active signs. *See also:* **Liquid crystals (/content/liquid-crystals/386300)**

Ceramics

Most ceramics contain large amounts of inorganic polymeric materials. While traditional ceramics were based on natural clays, today's ceramics generally are based on synthetic materials. Ceramics are generally brittle, strong, resistant to chemicals, and high-melting. The new high-temperature superconductors are ceramic material.

Cements

The term "cement" is used to describe a wide variety of materials, such as the adhesive materials used by dentists and the concrete (portland cement) used in constructing roads and buildings. Most cements are based on polymeric materials. *See also:* **Cement (/content/cement/118400)**

Smart materials

Most smart materials are polymeric. They are materials that react to an externally applied force (electrical, bending, pressure, temperature, light, magnetic), and then the interaction is used to achieve a defined engineering or scientific goal. Windows that regulate the amount of light that is transmitted through them as the amount of sunlight varies are an example of smart materials because the windows are part of a more complete energy-control system.

Additives

Processed polymeric materials are generally a combination of the polymer and the materials that are added to modify its properties, assist in processing, and introduce new properties. The latter materials are called additives.

Additives can be solids, liquids, or gases. Thus, for many latex paints, the polymer is poly(methyl methacrylate), titanium IV oxide is added as the pigment, and other materials are added to assist the paint to "cover" the surface, to protect the material from ultraviolet radiation degradation, and to help it resist mildew. *See also:* **Inhibitor (chemistry) (/content/inhibitor-chemistry/344900)**

Some typical additives are:

Antiblocking agents	Foaming agents
Antifoaming agents	Impact modifiers
Antifogging agents	Low-profile materials
Antimicrobial agents	Lubricants
Antioxidants	Mold release agents
Antistatic agents	Odorants/fragrances
Antizonates	Plasticizers
Blowing agents	Preservatives
Coloring agents	Reinforcements
Coupling agents	Slip agents
Curing agents	Softeners
Extenders	Stabilizers—radiation and heat
Fillers	Viscosity modifiers
Finishing aids	
Flame retardants	

Plasticizers

Plasticizers are added to increase the flexibility and to reduce the melt temperature range and viscosity. Most plasticizers can be considered to be near-solvents that allow segmental mobility to occur. In natural systems, water often acts as a plasticizer, allowing proteins, nucleic acids, and polysaccharides to be flexible. For synthetic polymers, most plasticizers are designed to be nonmobile and nonvolatile.

Antioxidants

Antioxidants are added to retard oxidative degradation generally brought about by the formation of free radicals through application of heat, ionizing radiation, or mechanical shear. *See also:* **Antioxidant (/content/antioxidant/041500)**

Colorants

Many materials contain colorants or coloring agents. Colorants are generally added to increase the esthetic value of a coating.

Fillers and reinforcements

Fillers are relatively inert materials, while reinforcements improve the properties of the material to which they have been added. For many composites, addition of reinforcing fibers produces dramatic improvements in the strength of the material. While most fillers are added to simply increase the bulk of the material, some provide needed increases in the mechanical properties of the material. Fillers are generally inexpensive, lightweight, and readily available in large quantity. Fillers include natural organic materials such as wood product discard materials, corncobs, and peanut shells. Glass of many forms as well as a number of minerals (including sand and diatomaceous earth, mica, and talc) are also used as fillers.

Recycling and Degradation

Polymers offer a wide variety of techniques for recycling and degradation. Recycling of simple polymeric materials such as bottles and containers is fairly straightforward. Many polymers are thermoplastics, that is, they can be reshaped through application of heat and pressure and used in the production of other thermoplastic materials. The recycling of thermosets, polymers that do not melt but degrade prior to softening, is more difficult. These materials are often ground into a fine powder, are blended with additives (often adhesives or binders), and then are reformed.

Most glass contains some reused glass, and much paper contains recycled paper.

The recycling of more complex objects such as tires is more difficult since they are composed of a number of different materials that must be separated before real recovery of the material is possible. *See also:* **Recycling technology (/content/recycling-technology/757456)**

The mechanism for the degradation of polymers can be divided into two general categories—biological and physical. Many microorganisms contain enzymes that are "sent out" by the organism to locate food and render it usable to the organism. Some of these organisms have enzymes that degrade the polar linkages that are present in polyesters, polyamides, and other condensation polymers. Thus, these polymers can be degraded by microorganisms. *See also:* **Biodegradation (/content/biodegradation/422025)**

Physical degradation includes "simple" hydrolysis (with catalysis by the acid found in acid rain), heat, and light. Again, condensation polymers are particularly sensitive to hydrolysis. Many vinyl polymers are degraded through exposure to light as well. *See also:* **Hydrolysis (/content/hydrolysis/329900)**

The Future

Materials in today's society must be varied to perform many tasks. Often they must perform them repeatedly and in a special manner. Plastic hinges must be able to work thousands of times. The human heart, a complex muscle largely made up of protein polymers, provides about 2.5 billion beats within a lifetime, moving oxygen throughout the approximately 144,000 km of a circulatory system and delivering about 8000 liters of blood daily with little deterioration of the cell walls. Nerve impulses travel within the body about 300 m per minute, and macromolecules are the materials that allow this rapid and precise transfer of nerve impulses. Bones are made of polymeric materials, and have a strength about five times that of steel on a weight basis. In this century, synthetic polymers should approach the properties of these biological polymers.

Polymers are part of the so-called nanorevolution where single polymer strands, one atom thick, will be the connectors; polymer sheets one molecule thick will act as adhesives and insulators for communication (including computers); small motors the breadth of 1/20th of a human hair will go from zero to 500,000 revolutions per second in a real "blink of an eye." *See also:* **Nanotechnology (/content/nanotechnology/757333)**

Catalysis for production of polymers and the use of polymers as catalysts continue. The presence of soluble stereoregulating catalysts used in the production of polymers will allow better control and enhanced properties for these materials. The use of polymers for multisite synthesis will continue to be developed. *See also:* **Catalysis and catalysts (/content/catalysis-and-catalysts/113200)**

The use of superstructures will continue, including in the mimicry of nature. For instance, the mucus of snails contains protein "ball-bearing-like" spheres: efforts are under way to mimic these proteins using synthetic polymeric materials. The synthesis of biomedical materials, including skin and tendons, will continue along with the creation of materials for replacement of structural body parts.

Manufacturing companies are dividing into those that produce bulk polymers on a large scale and others that produce specialty polymers on a smaller scale. The development, use, and production of specialty polymers for specific applications will increase. The use of, and improvement in properties of, the older "standby" polymers such as polyethylene will also continue.

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