# CHAPTER 27: POLYMERS

## Organic and Biochemistry Supplement to Enhanced Introductory College Chemistry

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## In this chapter, you will learn about:

- The two main processes of polymerization
- Different ways to classify polymers
- Properties of various polymers
- Common polymers and plastics
- The impact of plastics on the environment and how they are recycled

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Organic functional groups and their physical properties (Chapter 19: Organic Chemistry)
- Sigma and pi carbon-carbon bonds (Chapter 21.1 Valence Bond Theory)

Polymers are everywhere in our world: from the DNA that codes our bodies to the toys we play with to the medical equipment that provide lifesaving support. Even the foods we eat are formed of polymers. Can you think of where polymers are not used in our daily lives?

# Watch From DNA to Silly Putty: The diverse world of polymers – Jan Mattingly – YouTube (https://youtu.be/UwRVj9rz2QQ?) (5 min)

In this chapter, we will explore the formation of polymers and the different types of polymers. Plastics, a type of polymer, are everywhere and the impacts of plastics on our daily life, the environment, and our health are significant.

#### Watch A brief history of plastic – YouTube (https://youtu.be/9GMbRG9CZJw?) (5 min)

### Spotlight on Everyday Chemistry: Superglue, Kevlar, and Barbie

There are thousands of examples of polymers in our world. Here are just three that you may not have thought of.

#### Superglue

Superglue is a polymer. The original compound reacts with water from the air to form an adhesive polymer. Infographic 27.0a. shows some of the details on how superglue works.



Infographic 27.0a. The chemistry of superglue showing the cyanacrylates reaction with water to form an adhesive polymer. Read more about "Sticky Science – The Chemistry of Superglue (https://www.comp oundchem.com/ 2015/10/15/ superglue/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 27.0a [New tab].

#### Kevlar

Kevlar is probably best known for stopping bullets in the form of a vest, but it has many other applications as well. It is a polymer formed from two monomers (starting molecules). Infographic 27.0b. shows the structure and usages of Kevlar.



**Infographic 27.0b.** Kevlar – the polymer called polyparaphenylene terephthalamide used in bulletproof vests and other applications. Read more about "The Myriad Uses of Stronger Than Steel Kevlar" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 27.0b [New tab].

#### Barbie

Toys are a very common use of polymers and plastics. A Barbie doll is made of several different plastics in order to provide the desired textures and flexibility needed for the toy. Infographic 27.0c. shows some of the types of plastics used to make various parts of a Barbie doll.



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# 27.1 POLYMERIZATION

# Learning Objectives

By the end of this section, you will be able to:

- Define the terms monomer and polymer.
- Know some different examples of synthetic and natural polymers.

A **polymer** is a large molecule, or **macromolecule**, composed of many repeated subunits. The term "polymer" derives from the Greek word *polus* (meaning "many, much") and m*eros* (meaning "part") and refers to a molecule whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties. An example of a polymer is shown in Figure 27.1a.



**Figure 27.1a.** Polymer formation during a polymerization reaction, a large number of monomers become connected by covalent bonds to form a single long molecule, a polymer. (Credit left: *General Chemistry*, CC BY-NC-SA 3.0, right: Image by K.R Roshith, CC BY-SA 4.0)

Due to their broad range of properties, both **synthetic** and **natural** polymers play essential and ubiquitous roles in everyday life. Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created via **polymerization** of many small molecules, known as **monomers**. Their consequently large molecular mass relative to small molecule compounds produces unique physical

properties, including toughness, viscoelasticity, and a tendency to form glasses and semicrystalline structures rather than crystals. The terms polymer and resin are often synonymous with plastic.

## Natural Polymers

Some very important biological materials are polymers. Of the three major food groups, polymers are represented in two: proteins and carbohydrates. **Proteins** are polymers of amino acids, which are monomers that have an amine functional group and a carboxylic acid functional group. Proteins play a crucial role in living organisms.

Another example of a natural polymer involves linking hundreds of glucose molecules together to make a relatively common material known as **starch**. Starch is an important source of energy in the human diet. Note, in Figure 27.1b., how the individual glucose units are joined together to form starch.



**Figure 27.1b.** Polymer structure of starch with repeating glucose units. (Credit: *Introductory Chemistry*, CC BY-NC-SA 3.0)

Glucose molecules can also be joined together in another way, as shown in Figure 27.1c., to form a polymer known as cellulose. Cellulose forms the strands found in cotton that we use in clothing.





**Cellulose** is a major component in the cell walls of plants. Curiously, despite the similarity in the building blocks between starch and cellulose, some animals (such as humans) cannot digest cellulose; those animals

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that can digest cellulose typically rely on symbiotic bacteria in the digestive tract for the actual digestion. Animals do not have the proper enzymes to break apart the glucose units in cellulose, so it passes through the digestive tract and is considered dietary fiber.

**Deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)** are also polymers, composed of long, three-part chains consisting of phosphate groups, sugars with 5 C atoms (ribose or deoxyribose), and N-containing rings referred to as bases. Each combination of the three parts is called a nucleotide; DNA and RNA are essentially polymers of nucleotides that have rather complicated but intriguing structures (Figure 27.1d.). DNA is the fundamental material in chromosomes and is directly responsible for heredity, while RNA is an essential substance in protein synthesis. These natural polymers, or biopolymers (polymers produced by living organisms), are discussed further in Chapter 28.



**Figure 27.1d.** Nucleotides in DNA double helix (credit: animation by brian0918, PDM).

# Synthetic Polymers

Synthetic polymers are often formed from monomers derived from fossil fuels and petroleum products. Current research is focused on finding other more renewable sources of monomers.

# Celluloid: Billiard Balls

**Celluloids** are a class of compounds created from nitrocellulose (partially nitrated cellulose) and camphor, with added dyes and other agents. Generally considered the first thermoplastic, it was first created as Parkesinein (by Alexander Parkes of Birmingham England) in 1856 and as Xylonite in 1869. In the 1860s, an American, John Wesley Hyatt, acquired Parkes's patent and began experimenting with cellulose nitrate with the intention of manufacturing billiard balls, which until that time were made from ivory. In the 1870s the

modified plastic was registered as "celluloid". The formation and structure of celluloid is shown in Figure 27.1e.

The main use was in movie and photography film industries, which used only celluloid film stock prior to the adoption of acetate safety film in the 1950s. Celluloid is highly flammable, difficult and expensive to produce and no longer widely used; its most common uses today are in table tennis balls, musical instruments, and guitar picks.



**Figure 27.1e.** Billard balls representing the Bicentennial. (Credit right: work by MaChe, PDM; left: modification of work courtesy of the Gerald R. Ford Presidential Museum, PDM)

### Bakelite

Bakelite (sometimes spelled Baekelite) or polyoxybenzylmethylenglycolanhydride was the first plastic made from synthetic components. It is a thermosetting phenol formaldehyde resin, formed from a condensation reaction of phenol with formaldehyde. It was developed by the Belgian-American chemist Leo Baekeland in Yonkers, New York, in 1907.

Bakelite was patented on December 7, 1909. The creation of a synthetic plastic was revolutionary for its electrical non conductivity and heat-resistant properties in electrical insulators, radio and telephone casings and such diverse products as kitchenware, jewelry, pipe stems, children's toys, and firearms. Figure 27.1f. shows examples of products made from Bakelite.



**Figure 27.1f.** Examples of products made from Bakelite (**credit** a: "Set of Phenol formaldehyde resin buttons" by Gregory Tobias, CC BY-SA 3.0; b: work by William Warby (https://www.flickr.com/people/ 26782864@N00), CC BY 2.0; c: work by Tangerineduel, CC BY-SA 4.0).

#### Watch Polymers: Crash Course Chemistry #45 – YouTube (https://youtu.be/ rHxxLYzJ8Sw?) (10 min)

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- Wikipedia

# 27.2 CLASSIFICATION OF POLYMERS

## Learning Objectives

By the end of this section, you will be able to:

- Distinguish between thermoplastic and thermosetting polymers
- Distinguish between addition and condensation polymers

Polymers can be classified in two ways: based on their physical response to heating resulting in how they are used and based on their method of polymerization resulting from how they are prepared.

# **Plastics**

The term **plastics** is used to describe polymers that are capable of being molded (formed into a shape) or are pliable. (Hein et al., 2014)

# Thermoplastic and Thermosetting Polymers

Polymers are classified by their physical behaviour when heated. **Thermoplastic polymers** are soften when heated. They are plastics that become firm again when cooled. Thermoplastic polymers are common because the cycle of heating and cooling is common in the forming and recycling process and allows the polymer to be reformed. (Libretexts, 2022)

In thermoplastic polymers, monomer molecules are joined end to end in a linear chain with little to no cross linking between the chains. (Hein et al., 2014) In Figure 27.2a. and Figure 27.2b., the thermoplastic polymer (also called an elastomer in this image) shows multiple strands of polymer chains but no connection between any of the strands so the polymer can be stretched. Polyethylene is an example of a thermoplastic polymer. (Hein et al., 2014)



**Figure 27.2a.** Arrangement of polymer chains in a thermoplastic and thermosetting polymer. (Credit: Photo by LaurensvanLieshout, CC BY-SA 3.0)



**Figure 27.2b.** Schematic views: left, linear chains of macromolecules (case of a thermoplastic polymer); right, a three-dimensional macromolecule (case of a thermosetting polymer). The tri- and tetravalent cross-linking nodes are represented in black. Such a network is insoluble and does not melt. Dimension of a circle (monomer unit): approximately one ångström (Å). (Credit: Photo by Cjp24, CC BY-SA 3.0)

**Thermosetting polymers** soften when heated. They are plastics that can be molded but will harden permanently when cooled. If heated, thermosetting polymers will decompose. A common example is Bakelite commonly used in objects that require stiffness and some heat insensitivity such as toasters, pot handles, electrical components and billiard balls. (Libretexts, 2022) In a thermoplastic polymer, the polymer chains are cross linked resulting in an infusible solid.(Hein et al., 2014) Figure 27.2a. and 27.2b. show the structure of the polymer chains in a thermosetting polymer.

# **Addition and Condensation Polymers**

Addition polymerization and condensation polymerization are two modes of polymerization reactions in the formation of polymers.

In an **addition polymerization**, the monomer molecules bond to each other without the loss of any other atoms. Addition or chain-growth polymerization involves the rearrangement of bonds within the monomer in such a way that the monomers link up directly with each other. Figure 27.2c. shows the formation of ethylene through addition polymerization. Addition polymers from alkene monomers or substituted alkene monomers are the biggest groups of polymers in this class. Ring opening polymerization can occur without the loss of any small molecules.



**Figure 27.2c.** Addition polymerization of ethene (ethylene) to form polyethene (polyethylene). (Credit: Photo by V8rik, CC BY-SA 3.0).

In **condensation polymerization**, two different monomers combine with the loss of a small molecule, usually water. Most polyesters and polyamides (nylon) are in this class of polymers. Figure 27.2d. shows the condensation polymerization of Nylon 6,6. A large number of important and useful polymeric materials are not formed by addition polymerization, but proceed instead by conventional functional group transformations of polyfunctional reactants. These polymerizations often (but not always) occur with loss of a small byproduct, such as water, and generally (but not always) combine two different components in an alternating structure.





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# 27.3 POLYETHYLENE

### Learning Objectives

By the end of this section, you will be able to:

• Differentiate the types of polyethylene, especially LDPE and HDPE.

**Polyethylene** was first synthesized by the German chemist Hans von Pechmann, who prepared it by accident in 1898. Industrial production of low-density polyethylene (LDPE) began in 1939 in England. Because polyethylene was found to have very low-loss properties at very high frequency radio waves, commercial distribution in Britain was suspended on the outbreak of World War II in order to produce insulation for UHF (ultra high frequency) and SHF (super high frequency) cables of radar sets.

Polyethylene or polythene (PE) is the most common plastic. As of 2017, over 100 million tonnes of polyethylene resins are produced annually, accounting for 34% of the total plastics market. Its primary use is in packaging (plastic bags, plastic films, geomembranes, containers including bottles, etc.). Many kinds of polyethylene are known, with most having the chemical formula  $(C_2H_4)_n$ . PE is usually a mixture of similar polymers of ethylene with various values of n.

Polymers based on skeletons with only carbon are all synthetic. Let's begin by looking at polyethylene in Figure 27.3a. It is the simplest polymer, consisting of random-length (but generally very long) chains made up of two-carbon units.



**Figure 27.3a.** Structure and formation of polyethylene. (Credit: *Chemistry for Changing Times (Hill and McCreary)*, CC BY-SA )

You will notice some "fuzziness" in the way that the polyethylene structures are represented above. The squiggly lines at the ends of the long structure indicate that the same pattern extends indefinitely. The more

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compact notation on the right shows the minimal repeating unit enclosed in brackets overprinted with a dash; this means the same thing and is the preferred way of depicting polymer structures. In Figure 27.3b., various representations of polyethylene are shown.



**Figure 27.3b.** a) 3D representation of polyethylene, b) line structure representation of polyethylene, c) structural formula representation of polyethylene, d) 2D representation of polyethylene, e) photo of polyethylene beads. (credit a: "Polyethylene-3D" by Benjah-bmm27, PDM; b. "Polyethylene repeat unit" by Av wiki, PDM; c. "Chemical structural formula (repeat unit) of polyethylene" by Chem Sim 2001, PDM; d: "Polyethylene-repeat-2D" by Benjah-bmm27, PDM; e: "Polyethylene balls10" by Lluis tgn, CC BY-SA 3.0)

# Types of Polyethylene

Most synthetic polymers are formed from ethylene.

The relative lengths of the chains and any branches control the properties of polyethylene.

The most important polymer grades with regard to volume are High density polyethylene (HDPE) and Low

density polyethylene (LDPE). Other grades include Linear low density polyethylene (LLDPE) and Ultra high molecular weight polyethylene (UHMWPE) (Hein et al., 2014).

**HDPE (High density polyethylene)** is defined by a density of greater or equal to 0.941 g/cm<sup>3</sup>. HDPE has a low degree of branching. The mostly linear molecules pack together well, so intermolecular forces are stronger than in highly branched polymers. HDPE has high tensile strength. It is used in products and packaging such as milk jugs, detergent bottles, butter tubs, garbage containers, and water pipes. One-third of all toys are manufactured from HDPE. In 2007, the global HDPE consumption reached a volume of more than 30 million tons. HDPE is considered to have aligned polymer chains that support rigidity but can be brittle and crack under some circumstances (Hein et al., 2014).

# Watch What Is HDPE Plastic? | High-Density Polyethylene – YouTube (https://youtu.be/G8rPezOpjD0?) (2 min)

**LDPE (Low density polyethylene)** is defined by a density range of 0.910–0.940 g/cm<sup>3</sup>. LDPE has a high degree of short- and long-chain branching, which means that the chains do not pack into the crystal structure as well. It has, therefore, less strong intermolecular forces as the instantaneous-dipole induced-dipole attraction is less. This results in a lower tensile strength and increased ductility. The high degree of branching with long chains gives molten LDPE unique and desirable flow properties. LDPE is used for both rigid containers and plastic film applications such as plastic bags and film wrap. In 2013, the global LDPE market had a volume of almost US\$33 billion. LDPE is considered to have randomly packed polymer chains that support toughness and can stretch (Hein et al., 2014).

# Watch What Is LDPE Plastic? | Does Low-Density Polyethylene Really Get Recycled? – YouTube (https://youtu.be/b0vBaS7rbhk?) (2 min)

**LLDPE (Linear low density polyethylene)** is defined by a density range of 0.915–0.925 g/cm<sup>3</sup>. LLDPE is a substantially linear polymer with significant numbers of short branches. LLDPE has higher tensile strength than LDPE, and it exhibits higher impact and puncture resistance than LDPE. Lower thickness (gauge) films can be blown, compared with LDPE, with better environmental stress-cracking resistance, but is not as easy to process. LLDPE is used in packaging, particularly film for bags and sheets. Lower thickness may be used compared to LDPE. It is used for cable coverings, toys, lids, buckets, containers, and pipe. While other applications are available, LLDPE is used predominantly in film applications due to its toughness, flexibility, and relative transparency. Product examples range from agricultural films, Saran wrap, and bubble wrap, to multilayer and composite films. In 2013, the world LLDPE market reached a volume of US\$40 billion.

UHMWPE (Ultra high molecular weight polyethylene) has extra-long chains of polyethylene resulting in a stiff but less brittle plastic. (Hein et al., 2014)

Watch LDPE vs. HDPE: Similarities and Difference – YouTube (https://youtu.be/ mLjLl1ORSgg?) (2 min)

# Polyethylene Production

#### Watch Polythene production – YouTube (https://youtu.be/U6d\_F1jcKzI?) (4 mins)

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# References cited in text:

Hein, M., Pattison, S., Arena, S., & Best, L. R. (2014). *Introduction to General, Organic, and Biochemistry* (11th ed.). Wiley.

# 27.4 ADDITION POLYMERIZATION

## Learning Objectives

By the end of this section, you will be able to:

- Define addition polymerization.
- Draw the structure of a polymer from its monomer.
- Know the uses/applications of common addition polymers.

Addition polymerization is one method of forming polymers. In addition polymerization, the monomer molecules bond to each other without the loss of any other atoms. Addition polymers from alkene monomers or substituted alkene monomers are the biggest groups of polymers in this class. In some cases, addition polymerization can open a ring-based monomer without the loss of any small molecules.

# **Process of Addition Polymerization**

Addition or chain-growth polymerization involves the rearrangement of bonds within the monomer in such a way that the monomers link up directly with each other. This is represented in Figure 27.4a. where two monomers are covalently bonded together to form a dimer (two monomer units joined).



**Figure 27.4a.** Two monomers are covalently bonded together to form a dimer. (Credit: *Map: Chemistry for Changing Times (Hill and McCreary)*, CC BY-NC-SA 4.0)

In order to make this happen, an **initiator** (chemically active molecule) is needed to start what is known as a **chain reaction**. The manufacture of polyethylene is a very common example of such a process. It employs a

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**free-radical** initiator that donates its unpaired electron to the monomer, making the latter highly reactive and able to form a bond with another monomer at this site.

In theory, only a single chain-initiation process needs to take place, and the chain-propagation step then repeats itself indefinitely, but in practice multiple initiation steps are required, and eventually two radicals react to bring the polymerization to a halt. This is called **chain termination**. See the free radical chain mechanism in Figure 27.4b. As with all polymerizations, chains having a range of molecular weights are produced, and this range can be altered by controlling the pressure and temperature of the process.



**Figure 27.4b.** Free-radical mechanism for the formation of polyethylene. (Credit: *Map: Chemistry for Changing Times (Hill and McCreary)*, CC BY-NC-SA 4.0)

# Polyethylene Derivatives

Most common plastics and polymers are derived from modified ethylene monomers (Hein et al, 2014). Some common addition polymers are shown in Figure 27.4c. and Table 27.4a. Note that all the monomers have carbon-to-carbon double bonds. Many polymers are mundane (e.g., plastic bags, food wrap, toys, and tableware), but there are also polymers that conduct electricity, have amazing adhesive properties, or are stronger than steel but much lighter in weight.



**Figure 27.4c.** Some common addition polymers made from ethylene monomer derivatives. (Credit: *Map: Chemistry for Changing Times (Hill and McCreary)*, CC BY-NC-SA 4.0)

Monomer	Polymer Name	Trade Name(s)	Uses
H <sub>2</sub> C=CCl <sub>2</sub>	polyvinylidene dichloride	Saran	Clinging food wrap
H <sub>2</sub> C=CH(CN)	polyacrylonitrile	Orlon, Acrilan, Creslan	Fibers for textiles, carpets, upholstery
H <sub>2</sub> C=CH(OCOCH <sub>3</sub> )	polyvinyl acetate		Elmer's glue – Silly Putty Demo
H <sub>2</sub> C=CH(OH)	polyvinyl alcohol		Ghostbusters Demo
H <sub>2</sub> C=C(CH <sub>3</sub> )COOCH <sub>3</sub>	polymethyl methacrylate	Plexiglass, Lucite	Stiff, clear, plastic sheets, blocks, tubing, and other shapes
H <sub>2</sub> C=CH-C(CH <sub>3</sub> )=CH <sub>2</sub>	polyisoprene	natural or some synthetic rubber	applications similar to natural rubber
H <sub>2</sub> C=CH-CH=CH <sub>2</sub>	polybutadiene	polybutadiene synthetic rubber	select synthetic rubber applications
H <sub>2</sub> C=CH-CCl=CH <sub>2</sub>	polychloroprene	Neoprene	chemically-resistant rubber

Table 27.4a. More common addition polymers made from ethylene monomer derivatives.

 

 Table Source: "10.3: Addition Polymerization – One + One + One + One + ... Gives One!" In Map: Chemistry for Changing Times (Hill and McCreary), CC BY-NC-SA 4.0

#### Polypropylene

**Polypropylene (PP),** also known as polypropene, is a thermoplastic polymer used in a wide variety of applications. It is produced via chain-growth polymerization from the monomer propylene. Phillips Petroleum chemists J. Paul Hogan and Robert Banks first polymerized propylene in 1951. The orientation of the third carbon in the propylene monomer results in different version of polypropylene that vary in properties.

Propylene was first polymerized to a crystalline isotactic polymer by Giulio Natta as well as by the German chemist Karl Rehn in March 1954. Polypropylene is used alone or as a **copolymer**, usually with ethylene. These polymers have an exceptionally wide range of uses — rope, binder covers, plastic bottles, staple yarns, non-woven fabrics, electric kettles. When uncoloured, it is translucent but not transparent. Its resistance to fatigue makes it useful for food containers and their lids, and flip-top lids on bottled products such as ketchup.

After polyethylene, polypropylene is the most profitable plastic with revenues expected to exceed US\$145 billion by 2019. The sales of this material are forecast to grow at a rate of 5.8% per year until 2021. Polypropylene is produced by the chain-growth polymerization of propylene. Figure 27.4d. show the polymerization of polypropylene, the line structure of polypropylene, a 3D rendering of polypropylene and examples of materials made from polypropylene.



**Figure 27.4d.** a) the polymerization of polypropylene, b) the line structure of polypropylene, c) a 3D rendering of polypropylene and d) examples of materials made from polypropylene. (credit a: Image by Cjp24 translated by Vis M, PDM; b: Image by NEUROtiker, PDM; c: Image by Benjah-bmm27, PDM; d: Image by Joep Vogels, Textielmuseum Tilburg, CC BY-SA 4.0).

#### Polystyrene

Polystyrene was discovered in 1839 by Eduard Simon, an apothecary from Berlin. In 1941, Dow Chemical invented a Styrofoam process. Polystyrene is transparent but rather brittle, and yellows under UV light. Widely used for inexpensive packaging materials and "take-out trays", foam "packaging peanuts", CD cases, foam-walled drink cups, and other thin-walled and moldable parts.

Expanded polystyrene (EPS) is a rigid and tough, closed-cell foam with a normal density range of 11 to 32 kg/m<sup>3</sup>. It is usually white and made of pre-expanded polystyrene beads. EPS is used for food containers, molded sheets for building insulation, and packing material either as solid blocks formed to accommodate the item being protected or as loose-fill "peanuts" cushioning fragile items inside boxes. EPS is colloquially called "styrofoam" in the United States and Canada, an incorrectly applied genericization of Dow Chemical's brand of extruded polystyrene.

Polystyrene results when styrene monomers interconnect. In the polymerization, the carbon–carbon  $\pi$  bond of the vinyl group is broken and a new carbon–carbon  $\sigma$  bond is formed, attaching to the carbon of another styrene monomer to the chain. Figure 27.4e. shows the polymerization of polystyrene, the line structure of polystyrene and an example of materials made from polystyrene.



**Figure 27.4e.** a) the polymerization of polystyrene b) the line structure of polystyrene and c) an example of materials made from polystyrene. (credit a: Image by H Padleckas, PDM; b: Image by LordOider, PDM; c: Image by John Cross, CC BY-SA 4.0)

# Polyvinyl Chloride

PVC was accidentally synthesized in 1872 by German chemist Eugen Baumann. The polymer appeared as a white solid inside a flask of vinyl chloride that had been left exposed to sunlight. **Polyvinyl chloride (PVC)** is the world's third-most widely produced synthetic plastic polymer, after polyethylene and polypropylene. About 40 million tonnes are produced per year. Polyvinyl chloride is one of the world's most widely used polymers. By itself it is quite rigid and used in construction materials such as pipes, house siding, flooring. Addition of plasticizers make it soft and flexible for use in upholstery, electrical insulation, shower curtains and waterproof fabrics. There is some effort being made to phase out this polymer owing to environmental concerns. Figure 27.4f. shows the polymerization of vinyl chloride to form PVC as well as examples of PVC piping.





**Figure 27.4f.** The polymerization of vinyl chloride to form PVC and examples of PVC piping. (credit a: Image by Jü, PDM; b: Image by Nikat, CC BY-SA 3.0)

## Polytetrafluorethylene (PTFE): The Nonstick Coating

### Spotlight on Everyday Chemistry: Teflon



**Infographic 27.4a.** History of Teflon (PTFE). Read more about "Chemistry History: Teflon & Non-Stick Pans (https://www.compoundchem.com/2016/02/04/teflon/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 27.4a [New tab].

**Polytetrafluoroethylene (PTFE)** is a synthetic fluoropolymer of tetrafluoroethylene that has numerous applications. The best-known brand name of PTFE-based formulas is Teflon (Infographic 27.4a) Chemours, a spin-off of DuPont, originally discovered the compound in 1938. This highly crystalline fluorocarbon is exceptionally inert to chemicals and solvents. Water and oils do not wet it, which accounts for its use in cooking ware and other anti-stick applications, including personal care products.

These properties — non-adhesion to other materials, non-wetability, and very low coefficient of friction ("slipperyness") — have their origin in the highly electronegative nature of fluorine whose atoms partly shield the carbon chain. Fluorine's outer electrons are so strongly attracted to its nucleus that they are less available to participate in London (dispersion force) interactions.

#### Example 27.4a

Draw the polymer that results from the polymerization of tetrafluoroethylene.



(credit: Introductory Chemistry (V 1.0), CC BY-NC-SA 3.0)

#### Answer:

In the case of this monomer, the double bond opens up and joins to other monomers, just as with ethylene. The polymer that is made has this structure:



(credit: Introductory Chemistry (V 1.0), CC BY-NC-SA 3.0)

Exercise & Image credits: Introductory Chemistry (V 1.0), CC BY-NC-SA 3.0

### Exercise 27.4a

Draw the polymer that results from the polymerization of the following monomers. (Assume Si behaves the same as C)



**Exercise & Image (including solution images) credits:** *Introductory Chemistry (V 1.0)*, CC BY-NC-SA 3.0

Check Your Answers:<sup>1</sup>

Exercise 27.4b

In this image, identify which polymers are addition polymers. How are the other polymers formed?



Check Your Answers: <sup>2</sup>

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#### References cited in-text

Hein, M., Pattison, S., Arena, S., & Best, L. R. (2014). *Introduction to General, Organic, and Biochemistry* (11th ed.). Wiley.

### Notes

1. *a*.



b.



2. In the image, polyethene, polypropylene, polyvinyl chloride, polystyrene and polytetrafluoroethene are all addition polymers as they are derived from ethene (ethylene) based monomers. The other polymers are condensation polymers.

# 27.5 RUBBER AND OTHER ELASTOMERS

## Learning Objectives

By the end of this section, you will be able to:

- Acknowledge the history of rubber's discovery and commercialization.
- Know the properties of rubber.
- Describe the process of vulcanization.
- Describe synthetic rubber.

# Natural Rubber

Natural rubber, also called India rubber or *caoutchouc* consists of polymers of the organic compound isoprene. Isoprene is a butadiene monomer (two carbon-carbon double bonds in the molecule). Isoprene is 2-methyl-1,3-butadiene (Hein et al., 2014). These isoprene-based polymers along with minor impurities of other organic compounds and water form natural rubber. The rubber tree (*Castilla elastica*) (Figure 27.5a.) is a large tree indigenous to Central America. Its bark produces a stretchy material called latex ("Ancient Mesoamericans", 2020). The latex is a sticky, milky colloid drawn off by making incisions in the bark and collecting the fluid in vessels in a process called "tapping". The latex then is refined into rubber ready for commercial processing. Indigenous groups from Mesoamerica determined that mixing the latex from the rubber tree with the juice from the *Ipomoea alba* plant produced a firm bouncy solid ("Ancient Mesoamericans", 2020). In major areas, latex is allowed to coagulate in the collection cup. The coagulated lumps are collected and processed into dry forms for marketing. Thailand and Indonesia are currently two of the leading rubber producers in the world.



Figure 27.5a. Rubber (latex) collection from a rubber tree. (Credit: Photo by Vis M, CC BY-SA 4.0)

#### Indigenous Perspectives: Colonialism of Rubber

Learn more about the colonialized history of rubber.

Watch How Your Rubber Ducky Explains Colonialism – YouTube (https://youtu.be/ BWjzOcllxgM?) (7 min)

Forms of polyisoprene that are used as natural rubbers are classified as **elastomers**. Natural rubber is used extensively in many applications and products, either alone or in combination with other materials. In most of its useful forms, it has a large stretch ratio and high resilience, and is extremely waterproof.



```
Figure 27.5b. Structure of isoprene (2-methyl-1,3-butadiene) and the formation of cis-polyisoprene (rubber) (credit left: Image by Alhadis, PDM; middle Image by Nevetsjc using Inkscape, PDM; right: Image by Alhadis, Public Domain)
```

Molecules that have carbon-carbon double bonds can be subject to geometric isomerization. This is also true of polymers with carbon-carbon double bonds. Isoprene and other synthetic butadiene polymers can have cis and trans versions resulting in different spatial orientations and properties. Cis-polyisoprene (as shown in

Figure 27.5b.) is found in natural rubber. Trans-polyisoprene is called gutta-perch and is used in electrical insulation, dentistry and golf balls (Hein et al, 2014).

# **Vulcanization**

In 1832–1834 Nathaniel Hayward and Friedrich Ludersdorf discovered that rubber treated with sulfur lost its stickiness. It is likely Hayward shared his discovery with Charles Goodyear, possibly inspiring him to make the discovery of vulcanization. Thomas Hancock (1786–1865), a scientist and engineer, was the first to patent vulcanization of rubber. He was awarded a British patent on May 21, 1845. Three weeks later, on June 15, 1845, Charles Goodyear was awarded a patent in the United States. It was Hancock's friend William Brockedon who coined term 'vulcanization'. Goodyear claimed that he had discovered vulcanization earlier, in 1839.

**Sulfur vulcanization** is a chemical process for converting natural rubber or related polymers into more durable materials by heating them with sulfur or other equivalent curatives or accelerators. The term vulcanization is derived from Vulcan, the Roman god of fire. Sulfur forms cross-links (bridges) between sections of polymer chain which results in increased rigidity and durability, as well as other changes in the mechanical and electronic properties of the material. Vulcanization requires the presence of a carbon-carbon double bond in the polymer structure. The presence of the carbon-carbon double bond can result to age hardening and cracking of tires due to ozone attack. By vulcanizing the rubber, the useful temperature range of the rubber products and increases the abrasion resistance (Hein et al, 2014). A vast array of products are made with vulcanized rubber, including tires, shoe soles, hoses, and conveyor belts. Figure 27.5c. shows the ideal of sulfur cross-links and the chemical structure of vulcanized polyisoprene.



**Figure 27.5c.** Sketch of the impact of sulfur cross-links in polymers and general representation of the chemical structure of vulcanized natural rubber showing the crosslinking of two polymer chains (**blue** and **green**) with sulfur (n = 0, 1, 2, 3 ...). (credit left: Image by Cjp24, CC0; right: photo by Jü, CC0)

# Synthetic Rubber

The expanded use of bicycles, and particularly their pneumatic tires, starting in the 1880s, created increased demand for rubber. In 1909 a team headed by Fritz Hofmann, working at the Bayer laboratory in Germany,

succeeded in polymerizing isoprene, the first synthetic rubber. A synthetic rubber is any artificial elastomer. These are mainly polymers synthesized from petroleum byproducts.

**Polybutadiene** rubber is a polymer formed from the polymerization of the monomer 1,3-butadiene. Polybutadiene has a high resistance to wear and is used especially in the manufacture of tires, which consumes about 70% of the production. Another 25% is used as an additive to improve the toughness (impact resistance) of plastics such as polystyrene and acrylonitrile butadiene styrene (ABS). Polybutadiene rubber accounted for about a quarter of total global consumption of synthetic rubbers in 2012. It is also used to manufacture golf balls, various elastic objects and to coat or encapsulate electronic assemblies, offering high electrical resistivity. Figure 27.5d. shows the trans and cis versions of 1,4-polybutadiene



Figure 27.5d. Trans (left) and cis (right) -1,4-polybutadiene (credit Images a & b by Jü; CCO)

**Neoprene** (also polychloroprene or pc-rubber) is a family of synthetic rubbers that are produced by polymerization of chloroprene (2-chloro-1,3-butadiene). Neoprene exhibits good chemical stability and maintains flexibility over a wide temperature range. Neoprene is sold either as solid rubber or in latex form and is used in a wide variety of applications, such as laptop sleeves, orthopedic braces (wrist, knee, etc.), electrical insulation, liquid and sheet applied elastomeric membranes or flashings, and automotive fan belts. Neoprene is produced by free-radical polymerization of chloroprene. In commercial production, this polymer is prepared by free radical emulsion polymerization (Figure 27.4e.). Polymerization is initiated using potassium persulfate. Bifunctional nucleophiles, metal oxides (e.g. zinc oxide), and thioureas are used to crosslink individual polymer strands.



**Figure 27.4e.** Free radical synthesis of neoprene from 2-chloro-1,3-butadiene. (Credit: Photo by Rifleman 82, PDM)

Styrene-butadiene or **styrene-butadiene rubber (SBR)** describe families of synthetic rubbers derived from styrene and butadiene. SBR is an example of a **copolymer** where two different kind of monomer units are combined in a specific ratio (not necessarily 1:1) (Hein, 2014). Figure 27.4f. shows the structure of styrene-butadiene polymer showing repeating styrene (aromatic ring) and butadiene (carbon-carbon double bond) units. The version developed by Goodyear is called Neolite. These materials have good abrasion resistance and good aging stability when protected by additives. In 2012, more than 5.4 million tonnes of SBR were processed worldwide. About 50% of car tires are made from various types of SBR. It is a commodity material

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which competes with natural rubber. The elastomer is used widely in pneumatic tires. Other uses include shoe heels and soles, gaskets, and even chewing gum.



**Figure 27.4f.** Structure of styrene-butadiene polymer showing repeating styrene (aromatic ring) and butadiene (carbon-carbon double bond) units. (Credit: Photo by Smokefoot, CC BY-SA 3.0).

Spotlight on Everyday Chemistry: Athletic Tracks

Rubber and rubber like polymers are used in many places. Athletic running tracks are one example.



**Infographic 27.5a.** The application of rubber like polymers to athletic tracks. Read more about "What are the Olympics athletics tracks made of? (https://www.compoundchem.com/2021/08/07/athletics-track/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 27.5a [New tab].

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### References cited in text

Ancient Mesoamericans invented rubber 3,000 years before Goodyear. (2020, January 19). *History Daily.* Hein, M., Pattison, S., Arena, S., & Best, L. R. (2014). *Introduction to General, Organic, and Biochemistry* (11th ed.). Wiley.
# 27.6 CONDENSATION POLYMERS

## Learning Objectives

By the end of this section, you will be able to:

- Identify condensation polymerization.
- Identify some common condensation polymers and their properties and uses.

A large number of important and useful polymeric materials are not formed by addition polymerization but proceed instead by conventional functional group transformations of polyfunctional reactants. These polymerizations often occur with loss of a small byproduct, such as water, and generally combine two different components in an alternating structure. The polyester Dacron and the polyamide Nylon 66 are two examples of synthetic condensation polymers.

**Condensation polymerization** (also known as step-growth) requires that the monomers possess two or more kinds of functional groups that are able to react with each other in such a way that parts of these groups combine to form a small molecule (often  $H_2O$ ) which is eliminated from the two pieces (Figure 27.6a.). The now-empty bonding positions on the two monomers can then join together.



Figure 27.6a. Condensation polymerization reaction. (Credit: chem1, CC BY-SA 3.0).

In contrast to addition polymerization, most of which grow by carbon-carbon bond formation, step-growth polymers generally grow by carbon-heteroatom bond formation (C-O & C-N in Dacron & Nylon respectively). Although polymers of this kind might be considered to be alternating copolymers, the repeating monomeric unit is usually defined as a combined moiety.

Examples of naturally occurring condensation polymers are cellulose, starch, the polypeptide chains of

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proteins, and poly(β-hydroxybutyric acid), a polyester synthesized in large quantity by certain soil and water bacteria. See Chapter 28 for more information on biological molecules.

#### Indigenous Perspectives: Inuit Materials

Through thousands of years living in the Arctic, Inuit have learned to use resources that the land provides. Many key materials such as animal skins and wood are derived from polymer based chemical structures.

Animal skin contains collagen (Figure 27.6b.) which is a protein formed from amino acid units. Each amino acid is joined to the next amino acid through a condensation reaction. Animal skin also contains muco-polysaccharide which is a condensation polymer made with sugar and amino-sugar molecules (Figure 27.6c.) (Nagitarvik, & Rayner-Canham, 2022).



**Figure 27.6b.** Detail of collagen Gly-Pro-hPro triple helix, with backbone hydrogen bonds (credit: Image by Dcrjsr, CC BY 3.0).



**Figure 27.6c.** Skeletal formula of muco-polysaccharide chain (credit: Image by Vaccinationist, PDM).

Wood contains cellulose is a condensation polymer made from repeating sugar units. Cellulose provides a rigid framework to wood (Figure 27.6d.).



**Figure 27.6d.** Interconnected structure of cellulose based on repeating sugar units. This is another condensation polymer (credit: Image by Laghi.I, CC BY-SA 3.0).

For more information, read Composites in Inuit Life | Chem 13 News Magazine | University of Waterloo (uwaterloo.ca) (https://uwaterloo.ca/chem13-news-magazine/fall-2022-special-edition/feature/composites-inuit-life).

There are four main classes of condensation polymers: polyamides, polyesters, phenolics and polyurethanes (Hein et al, 2014).

# Polyamides including Nylon

Polyamides, such as nylons, Kevlar (see Chapter 27 introduction) and proteins, are an important class of condensation polymers. They arise from the reaction of carboxylic acid and an amine. When prepared from diamines and dicarboxylic acids, the polymerization produces two molecules of water per repeat unit.

 $n H_2N-X-NH_2 + n HO_2C-Y-CO_2H \rightarrow [HN-X-NHC(O)-Y-C(O)]_n + 2n H_2O$ The production of nylon 66 is an example of this process (Figure 27.6e. and 27.6f.). Note that the monomeric units that make up the polymer are not identical with the starting components.







**Figure 27.6f.** Synthesis of nylon highlighting the peptide bond (amide link) (credit *Chemistry for Changing Times (Hill and McCreary)*, CC BY-NC-SA 4.0).

Nylon is a thermoplastic silky material that can be melt-processed into fibers, films, or shapes. It is made of repeating units linked by amide links similar to the peptide bonds in proteins. Nylon polymers can be mixed with a wide variety of additives to achieve many different property variations. Nylon polymers have found significant commercial applications in fabric and fibers (apparel, flooring and rubber reinforcement), in shapes (molded parts for cars, electrical equipment, etc.), and in films (mostly for food packaging).

Nylon was the first commercially successful synthetic thermoplastic polymer. DuPont began its research project in 1927. The first example of nylon (nylon 6,6) was produced using diamines on February 28, 1935, by Wallace Hume Carothers (Figure 27.6d.). In response to Carothers' work, Paul Schlack at IG Farben developed nylon 6, a different molecule based on caprolactam, on January 29, 1938 (Figure 27.6g.). Notice that this already contains an amide link. When this molecule polymerizes, the ring opens, and the molecules join up in a continuous chain. Nylon 6 fibers are tough, possessing high tensile strength, as well as elasticity and lustre. They are wrinkleproof and highly resistant to abrasion and chemicals such as acids and alkalis. The fibers can absorb up to 2.4% of water, although this lowers tensile strength.

**TODAY IN CHEMISTRY HISTORY** 

27TH APRIL - WALLACE CAROTHERS' BIRTHDAY



**Infographic 27.6a.** History of nylon discovered by Wallace Carothers. Read more about "Chemistry History – Carothers, Condensation Polymerisation, & Nylon (https://www.compoundchem.com/2016/04/27/nylon/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 27.6a [New tab].



Figure 27.6g. Structure of caprolactam. (Credit: Supplemental Modules (Organic Chemistry), CC BY-NC 4.0)

Nylon was first used commercially in a nylon-bristled toothbrush in 1938, followed more famously in women's stockings or "nylons" which were shown at the 1939 New York World's Fair and first sold commercially in 1940. During World War II, almost all nylon production was diverted to the military for use in parachutes and parachute cord. Wartime uses of nylon and other plastics greatly increased the market for the new materials.

Kevlar is similar in structure to nylon-6,6 except that instead of the amide links joining chains of carbon atoms together, they join benzene rings. The two monomers are benzene-1,4-dicarboxylic acid and 1,4-diaminobenzene (Figure 27.6h.). If you line these up and remove water between the -COOH and -NH<sub>2</sub> groups in the same way as we did with nylon-6,6, you get the structure of Kevlar (Figure 27.6i.).





**Figure 27.6i.** Structure of Kevlar (Credit: *Supplemental Modules (Organic Chemistry)*, CC BY-NC 4.0)

Kevlar is a registered trademark of DuPont. Kevlar's first commercial use was as a replacement for steel in racing tires. Kevlar is typically spun into ropes or fibres. The material has a high tensile strength-to-weight ratio (it is about 5 times stronger than an equal weight of steel), making it useful for many applications from

bicycle tires to sails to body armour. The material owes much of its strength to hydrogen bonds between polymer chains. These bonds form between the carbonyl group oxygen atom (which has a partial negative charge due to oxygen's electronegativity) on one monomer and the partially positively charged hydrogen atom in the N–H bond of an adjacent monomer in the polymer structure (see dashed line in Figure 27.6j.). There is additional strength derived from the interaction between the unhybridized *p* orbitals in the six-membered rings, called aromatic stacking.



**Figure 27.6j.** The diagram shows the polymer structure of Kevlar, with hydrogen bonds between polymer chains represented by dotted lines (Credit: *Chemistry (OpenStax)*, CC BY 4.0).

Kevlar may be best known as a component of body armour, combat helmets, and face masks. Since the 1980s, the US military has used Kevlar as a component of the PASGT (personal armour system for ground troops) helmet and vest. Kevlar is also used to protect armoured fighting vehicles and aircraft carriers. Civilian applications include protective gear for emergency service personnel such as body armour for police officers and heat-resistant clothing for fire fighters. Kevlar based clothing is considerably lighter and thinner than equivalent gear made from other materials (Figure 27.6k.). In addition to its better-known uses, Kevlar is also often used in cryogenics for its very low thermal conductivity (along with its high strength). Kevlar maintains its high strength when cooled to the temperature of liquid nitrogen (-196 °C).



**Figure 27.6k.** (a) These soldiers are sorting through pieces of a Kevlar helmet that helped absorb a grenade blast. Kevlar is also used to make (b) canoes and (c) marine mooring lines. (credit a: modification of work by Michael T. Gams, USMC, PDM; credit b: Photo by OakleyOriginals, CC BY 2.0; credit c: modification of work by Casey H. Kyhl, PDM)

# Polyesters including Polyethylene Terephthalate

**Polyesters**, such as Dacron, are another important condensation polymer. They arise from the reaction of carboxylic acid and an alcohol.

n HO-X-OH + n HO<sub>2</sub>C-Y-CO<sub>2</sub>H →  $[O-X-O_2C-Y-C(O)]_n$  + (3n-2) H<sub>2</sub>O

The synthesis of Dacron (a polyester) is shown in Figure 27.6l. **Polyethylene terephthalate** (sometimes written poly(ethylene terephthalate)), commonly abbreviated PET, PETE, or the obsolete PETP or PET-P, is the most common thermoplastic polymer resin of the polyester family and is used in fibres for clothing, containers for liquids and foods, thermoforming for manufacturing, and in combination with glass fibre for engineering resins. PETE is recycling code number 1.



**Figure 27.6I.** The synthesis of Dacron/PETE (a polyester). (Credit: Virtual Textbook of Organic Chemistry, edited by Chemistry for Changing Times (Hill and McCreary), CC BY-NC-SA 4.0)

The majority of the world's PET production is for synthetic fibers (in excess of 60%), with bottle production accounting for about 30% of global demand. In the context of textile applications, PET is referred to by its common name, polyester, whereas the acronym PET is generally used in relation to packaging. Polyester makes up about 18% of world polymer production and is the fourth-most-produced polymer after polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC).

# Phenolics including Phenol-Formaldehyde and Related Resins

**Phenolics** are polymers made from phenol (hydroxybenzene). Bakelite is a phenolic polymer made from phenol and formaldehyde (methanal). It is a thermosetting polymer with extensive cross linking between polymer strands (Hein et al, 2014). Bakelite (Figure 26.7m.) was patented on December 7, 1909. The creation of a synthetic plastic was revolutionary for its electrical nonconductivity and heat-resistant properties in electrical insulators, radio and telephone casings and such diverse products as kitchenware, jewelry, pipe stems, children's toys, and firearms. In recent years the "retro" appeal of old Bakelite products has made them collectible. Bakelite was designated a National Historic Chemical Landmark on November 9, 1993, by the American Chemical Society in recognition of its significance as the world's first synthetic plastic.





**Figure 27.6m.** 3D structure of Bakelite (phenol-formaldehyde polymer). (Credit: Photo by JohnSRoberts99, GNU License, edited by *Chemistry for Changing Times (Hill and McCreary)*, CC BY-NC-SA 4.0).

Melamine (Figure 27.6n.) is an organic compound with the formula C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>. This white solid is a trimer of cyanamide, with a 1,3,5-triazine skeleton. Like cyanamide, it contains 67% nitrogen by mass, and its derivatives have fire retardant properties due to its release of nitrogen gas when burned or charred. Melamine can be combined with formaldehyde and other agents to produce melamine resins. Such resins are characteristically durable thermosetting plastic used in high pressure decorative laminates such as Formica, melamine dinnerware, laminate flooring, and dry erase boards. Melamine foam is used as insulation, soundproofing material and in polymeric cleaning products, such as Magic Eraser.



**Figure 27.6n.** Structure of Melamine.(Credit: Photo by User:Edgar181, PDM, edited by *Chemistry for Changing Times (Hill and McCreary)*, CC BY-NC-SA 4.0).

## Polyurethanes

**Polyurethane** (PUR and PU) is a polymer composed of organic units joined by carbamate (urethane) links. While most polyurethanes are thermosetting polymers that do not melt when heated, thermoplastic

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polyurethanes are also available. Polyurethanes are in the class of compounds called reaction polymers, which include epoxies, unsaturated polyesters, and phenolics. Polyurethanes are produced by reacting an isocyanate containing two or more isocyanate groups per molecule  $(R-(N=C=O)_n)$  with a polyol containing on average two or more hydroxyl groups per molecule  $(R'-(OH)_n)$  in the presence of a catalyst or by activation with ultraviolet light (Figure 27.60.).



Figure 27.60. Synthesis of polyurethane. (Credit: Photo by Hbf878. CC BY-SA 3.0)

Polyurethanes are used in the manufacture of high-resilience foam seating, rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires (such as roller coaster, escalator, shopping cart, elevator, and skateboard wheels), automotive suspension bushings, electrical potting compounds, high performance adhesives, surface coatings and surface sealants, synthetic fibers (e.g., Spandex), carpet underlay, hard-plastic parts (e.g., for electronic instruments), condoms, and hoses.

Fully reacted polyurethane polymer is chemically inert. No exposure limits have been established in the U.S. by OSHA (Occupational Safety and Health Administration) or ACGIH (American Conference of Governmental Industrial Hygienists). It is not regulated by OSHA for carcinogenicity. However, polyurethane polymer is a combustible solid and can be ignited if exposed to an open flame. Decomposition from fire can produce significant amounts of carbon monoxide and hydrogen cyanide, in addition to nitrogen oxides, isocyanates, and other toxic products. Because of the flammability of the material, it has to be treated with flame retardants (at least in case of furniture), almost all of which are considered harmful. California later issued Technical Bulletin 117 2013 which allowed most polyurethane foam to pass flammability tests without the use of flame retardants. Green Science Policy Institute states: "Although the new standard can be met without flame retardants, it does NOT ban their use. Consumers who wish to reduce household exposure to flame retardants can look for a TB117-2013 tag on furniture and verify with retailers that products do not contain flame retardants." Liquid resin blends and isocyanates may contain hazardous or regulated components. Isocyanates are known skin and respiratory sensitizers. Additionally, amines, glycols, and phosphate present in spray polyurethane foams present risks. Exposure to chemicals that may be emitted during or after application of polyurethane spray foam (such as isocyanates) are harmful to human health and therefore special precautions are required during and after this process.

In the United States, additional health and safety information can be found through organizations such as the Polyurethane Manufacturers Association (PMA) and the Center for the Polyurethanes Industry (CPI), as well as from polyurethane system and raw material manufacturers. Regulatory information can be found in the Code of Federal Regulations Title 21 (Food and Drugs) and Title 40 (Protection of the Environment). In Europe, health and safety information is available from ISOPA, the European Diisocyanate and Polyol Producers Association.

## **Polycarbonates**

**Polycarbonates** (PC) are a group of thermoplastic polymers containing carbonate groups (-O-(C=O)-O-) in their chemical structures. The main polycarbonate material is produced by the reaction of bisphenol A (BPA) and phosgene COCl<sub>2</sub>. The overall reaction is shown in Figure 27.6p.

Polycarbonates used in engineering are strong, tough materials, and some grades are optically transparent. They are easily worked, molded, and thermoformed. Because of these properties, polycarbonates find many applications. A balance of useful features, including temperature resistance, impact resistance and optical properties, positions polycarbonates between commodity plastics and engineering plastics.



**Figure 27.6p.** Formation of polycarbonate from bisphenol A and phosgene. (Credit: Photo by Akane700, PDM)

Polycarbonate is mainly used for electronic applications that capitalize on its collective safety features. Being a good electrical insulator and having heat-resistant and flame-retardant properties. The second largest consumer of polycarbonates is the construction industry, e.g., for dome lights, flat or curved glazing, and sound walls, which all use extruded flat solid or multiwall sheet, or corrugated sheet. A major application of polycarbonate is the production of Compact Discs, DVDs, and Blu-ray Discs.

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- "18.4 Amines and Amides" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/ 1-introduction)*

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# 27.7 PROPERTIES OF POLYMERS

## Learning Objectives

By the end of this section, you will be able to:

- Describe the physical properties of polymers based on their molecular and intermolecular structures.
- Identify crystalline and amorphous sections of polymers.
- Describe the processing of polymers.

# **Physical Properties**

The physical properties of a polymer such as its strength and flexibility depend on:

- **chain length** in general, the longer the chains the stronger the polymer;
- **side groups** polar side groups (including those that lead to hydrogen bonding) give stronger attraction between polymer chains, making the polymer stronger;
- **branching** straight, unbranched chains can pack together more closely than highly branched chains, giving polymers that have higher density, are more crystalline and therefore stronger;
- **cross-linking** if polymer chains are linked together extensively by covalent bonds, the polymer is harder and more difficult to melt.

#### Example 27.7a

Polymers are used in many toys such as Lego. Over time, the type of polymer used in Lego has changed. Infographic 27.7a. shows the polymer details of some Lego pieces.



**Infographic 27.7a.** The polymers of Lego. Read more about "What are Lego bricks made of, and why is treading on them so painful? (https://www.compoundchem.com/2018/04/09/lego/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 27.7a [New tab].

# **Crystalline and Amorphous Polymers**

When applied to polymers, the term crystalline has a somewhat ambiguous usage. A synthetic polymer may be loosely described as crystalline if it contains regions of three-dimensional ordering on atomic (rather than macromolecular) length scales, usually arising from intramolecular folding and/or stacking of adjacent chains as shown in Figure 27.7a.

Synthetic polymers may consist of both crystalline (aligned) and amorphous (random) regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material. Few synthetic polymers are entirely crystalline. The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer.

Polymers with crystalline regions are generally tougher (can be bent more without breaking) and more

impact-resistant than totally amorphous polymers. Polymers with a degree of crystallinity approaching zero or one will tend to be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to light scattering by crystalline or glassy regions.



**Figure 27.7a.** The crystalline parts of this polymer are shown in blue. (Credit: *Virtual Textbook of Organic Chemistry*, CC BY-NC-SA 4.0)

Depending on the degree of crystallinity, there will be a higher melting point at which the crystalline regions come apart and the material becomes a viscous liquid. These are thermoplastic polymers. Such liquids can easily be injected into molds to manufacture objects of various shapes or extruded into sheets or fibers.

Thermosetting polymers (generally those that are highly cross-linked) do not melt at all. If they are to be made into molded objects, the polymerization reaction must take place within the molds — a far more complicated process. About 20% of the commercially produced polymers are thermosets; the remainder are thermoplastics.

## **Glass Transition Temperature**

In thermoplastic polymers, there is a fairly definite softening point that is observed when the thermal kinetic energy becomes high enough to allow internal rotation to occur within the bonds and to allow the individual molecules to slide independently of their neighbours. This renders the polymer more flexible and deformable. This temperature is called the **glass transition temperature**.

Hard plastics like polystyrene and poly(methyl methacrylate) are used well below their glass transition temperatures, in their glassy state. Their glass transition temperatures are well above room temperature, both at around 100 °C. Rubber elastomers like polyisoprene and polyisobutylene are used above their glass transition temperature, that is, in the rubbery state, where they are soft and flexible.

# **Processing Polymers**

**Molding** is the process of manufacturing by shaping liquid or pliable raw material using a rigid frame called a mold or matrix. This itself may have been made using a pattern or model of the final object.

Compression molding is a forming process in which a plastic material is placed directly into a heated

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metal mold then is softened by the heat and therefore forced to conform to the shape of the mold, as the mold closes.

**Transfer molding** (BrE moulding) is a manufacturing process where casting material is forced into a mold. Transfer molding is different from compression molding in that the mold is enclosed rather than open to the fill plunger resulting in higher dimensional tolerances and less environmental impact.

**Injection molding** is a manufacturing process for producing parts by injecting molten material into a mold. Injection molding can be performed with a host of materials mainly including metals (for which the process is called die-casting), glasses, elastomers, confections, and most commonly thermoplastic and thermosetting polymers.

**Extrusion** is a process used to create objects of a fixed cross-sectional profile. A material is pushed through a die of the desired cross-section.

**Drawing** is a similar process, which uses the tensile strength of the material to pull it through the die. This limits the amount of change which can be performed in one step, so it is limited to simpler shapes, and multiple stages are usually needed. Drawing is the main way to produce wire. Metal bars and tubes are also often drawn.

#### Example 27.7b

#### **Medical Uses of Polymers**



**Figure 27.7b.** Hip Joint Replacement. Synthetic polymers are an important part of a hip joint replacement. The hip is much like a ball-and-socket joint, and total hip replacements mimic this with a metal ball that fits in a plastic cup. (Credits: *Introduction to Chemistry: GOB (V. 1.0).*, CC BY-NC-SA 3.0), edited by *(Ball et al.)*, CC BY-NC-SA 4.0.).

An interesting use of polymers is the replacement of diseased, worn out, or missing parts in the body. For example, about a 250,000 hip joints and 500,000 knees are replaced in US hospitals each year. The artificial ball-and-socket hip joints are made of a special steel (the ball) and plastic (the socket). People crippled by arthritis or injuries gain freedom of movement and relief from pain. Patients with heart and circulatory problems can be helped by replacing worn out heart valves with parts based on synthetic polymers. These are only a few of the many biomedical uses of polymers. **Example 27.7b source:** *Map: Chemistry for Changing Times (Hill and McCreary)* by LibreTexts, licensed under CC BY-NC-SA 4.0.

# Fiber Formation and Use

## Nylon

Bill Pittendreigh, DuPont, and other individuals and corporations worked diligently during the first few months of World War II to find a way to replace Asian silk and hemp with nylon in parachutes. It was also used to make tires, tents, ropes, ponchos, and other military supplies. It was even used in the production of a high-grade paper for U.S. currency. At the outset of the war, cotton accounted for more than 80% of all fibers used and manufactured, and wool fibers accounted for nearly all of the rest. By August 1945, manufactured fibers had taken a market share of 25%. After the war, with the of shortages of both silk and nylon, nylon parachute material was sometimes repurposed to make dresses. Nylon fibers are used in carpet manufacturing, tire cord and in tires.



**Figure 27.7c.** Blue nylon fabric ball gown. (Credit: Photo by Science History Institute, CC BY-SA 3.0)

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### Polyester

Fabrics woven or knitted from polyester thread or yarn are used extensively in apparel (Figure 27.7d.) and home furnishings, from shirts and pants to jackets and hats, bed sheets, blankets, upholstered furniture and computer mouse mats. Polyester fabrics are highly stain resistant. Industrial polyester fibers, yarns and ropes are used in car tire reinforcements, fabrics for conveyor belts, safety belts, coated fabrics and plastic reinforcements with high-energy absorption. Polyester fiber is used as cushioning and insulating material in pillows, comforters and upholstery padding.



**Figure 27.7d.** Stretching polyester fabric.. (Credit: Photo by Bearas, CC BY-SA 4.0)

#### Acrylics

Acrylic fibers are synthetic fibers made from a polymer (polyacrylonitrile) with an average molecular weight of -100,000, about 1900 monomer units. For a fiber to be called "acrylic" in the US, the polymer must contain at least 85% acrylonitrile monomer. Typical comonomers are vinyl acetate or methyl acrylate. DuPont created the first acrylic fibers in 1941 and trademarked them under the name Orlon. It was first developed in the mid-1940s but was not produced in large quantities until the 1950s. Strong and warm, acrylic fiber is often used for sweaters and tracksuits and as linings for boots and gloves, as well as in furnishing fabrics and carpets. It is manufactured as a filament, then cut into short staple lengths similar to wool hairs, and spun into yarn.

Modacrylic is a modified acrylic fiber that contains at least 35% and at most 85% acrylonitrile monomer. The comonomers vinyl chloride, vinylidene chloride or vinyl bromide used in modacrylic give the fiber flame retardant properties. End-uses of modacrylic include faux fur, wigs, hair extensions and protective clothing.

#### Microfibers

**Microfiber** (or microfibre) is synthetic fiber finer than one denier or decitex/thread, having a diameter of less than ten micrometers. This is smaller than the diameter of a strand of silk (which is approximately one denier), which is itself about 1/5 the diameter of a human hair (Figure 27.7e.).





The most common types of microfibers are made from polyesters, polyamides (e.g., nylon, Kevlar, Nomex, trogamide), or a conjugation of polyester, polyamide, and polypropylene. Microfiber is used to make mats, knits, and weaves for apparel, upholstery, industrial filters, and cleaning products. The shape, size, and combinations of synthetic fibers are selected for specific characteristics, including softness, toughness, absorption, water repellency, electrostatics, and filtering capabilities.

Microfiber textiles tend to be flammable if manufactured from hydrocarbons (polyester) or carbohydrates (cellulose) and emit toxic gases when burning, more so if aromatic (PET, PS, ABS) or treated with halogenated flame retardants and azo dyes. Their polyester and nylon stock are made from petrochemicals, which are not a renewable resource and are not biodegradable. However, if made out of polypropylene, they are recyclable (Prolen).

For most cleaning applications they are designed for repeated use rather than being discarded after use. An exception to this is the precise cleaning of optical components where a wet cloth is drawn once across the object and must not be used again as the debris collected are now embedded in the cloth and may scratch the optical surface.

Microfiber products may also have the potential of entering the oceanic water supply and food chain similar to other microplastics. Synthetic clothing made of microfibers that are washed can release materials and travel to local wastewater treatment plants, contributing to plastic pollution in water. Fibers retained in wastewater treatment sludge (biosolids) that are land-applied can persist in soils. A study by the clothing brand Patagonia and University of California, Santa Barbara, found that when synthetic jackets made of microfibers are washed, on average 1.7 grams (0.060 oz) of microfibers are released from the washing machine. These microfibers then travel to local wastewater treatment plants, where up to 40% of them enter into rivers, lakes, and oceans where they contribute to the overall plastic pollution. Microfibers account for 85% of manmade debris found on shorelines worldwide.

No pesticides are used for producing synthetic fibers in comparison to cotton. If these products are made

of polypropylene yarn, the yarn is dyed without any use of water compared to dying cotton, where thousands of liters of water become contaminated.

# **Attribution & References**

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# 27.8 PLASTICS AND RECYCLING

#### Learning Objectives

By the end of this section, you will be able to:

- Identify the type of polymer associated with each recycling number.
- Describe some different plastic recycling processes.

## **Recyclable Plastics**

Seven groups of plastic polymers, each with specific properties, are used worldwide for packaging applications (see Table 27.8a.). Each group of plastic polymers can be identified by its plastic identification code (PIC), usually a number or a letter abbreviation (Figure 27.8a.). For instance, low-density polyethylene can be identified by the number "4" or the letters "LDPE". The PIC appears inside a three-chasing-arrow recycling symbol. The symbol is used to indicate whether the plastic can be recycled into new products. These symbols can vary with producer and country.

The PIC was introduced by the Society of the Plastics Industry, Inc., to provide a uniform system for the identification of various polymer types and to help recycling companies separate various plastics for reprocessing. Manufacturers of plastic products are required to use PIC labels in some countries/regions and can voluntarily mark their products with the PIC where there are no requirements. Consumers can identify the plastic types based on the codes usually found at the base or at the side of the plastic products, including food/chemical packaging and containers. Not all categories are accepted by all local recycling authorities, so residents need to be informed about which kinds should be placed in recycling containers and which should be combined with ordinary trash.



**Figure 27.8a.** Plastic identification codes (PIC) and types of plastic (Credit: Image by juicy\_fish on Freepik).

Table 27.8a. The Major (





**Source:** Except where otherwise noted, this table is adapted from "Plastic recycling" and "Resin identification code" on Wikipedia, licensed under CC BY-SA 4.0; edited by Samantha Sullivan Sauer with reference to Hein et al (2014). Except where otherwise noted, all images are in the Public Domain. Image credits for plastic identification code in column 1: 06-PS Image by Anton Poliakov, CC BY-SA 4.0; 07-O Image by Tomia, CC

Often, products may be marked with a recycling symbol with number 7 or other numbers. These plastics are not standardized and as such are not recyclable in municipal process. The specific polymer is sometimes indicated but not always resulting in mixed plastics.

To see a summary of various plastics and those that are recyclable, refer to Figure 27.8b.



**Figure 27.8b.** Summary of plastics and those that are recyclable. (Credit: Image by Orion Lawlor, CCO)

Watch What Numbers of Plastic are Recyclable? – YouTube (https://youtu.be/jJlqyTb-oy0?) (2 mins)

# **Recycling Process**

Because plastics are largely non-biodegradable, the huge quantity (one estimate is 10<sup>8</sup> metric tons per year) of plastic materials produced for consumer and industrial use has created a gigantic problem of what to do with plastic waste. Plastics are difficult to incinerate safely and threaten to overwhelm the capacity of landfills (Figure 27.8c). An additional consideration is that production of most of the major polymers consumes non-renewable hydrocarbon resources.



**Figure 27.8c.** Plastic water bottles present a special recycling problem because of their widespread use in away-from-home locations. (Credit: Image by Celinebj, CC BY-SA 4.0)

Plastics recycling has become a major industry, greatly aided by enlightened trash management policies in the major developed nations. However, it is plagued with some special problems of its own:

- Recycling is only profitable when there is a market for the regenerated material. Such markets vary with the economic cycle. They practically disappeared during the recession that commenced in 2008.
- The energy-related costs of collecting and transporting plastic waste, and especially of processing it for re-use, are frequently the deciding factor in assessing the practicability of recycling.
- Collection of plastic wastes from diverse sources and locations and their transport to processing centers consumes energy and presents numerous operational problems.
- Most recycling processes are optimized for particular classes of polymers. The diversity of plastic types
  necessitates their separation into different waste streams usually requiring manual (i.e., low-cost)
  labor. This in turn encourages shipment of these wastes to low-wage countries, thus reducing the
  availability of recycled materials in the countries in which the plastics originated.

In general, plastics are collected and transported to a facility where they are sorted by recycling code. This is one of the major limiting factors of the process. There are several ways the plastics are separated including by hand, through physical property comparison and using technology. The plastics are then shredded, washed, and granulated into pellets. These pellets are then transported and reformed into future products. Products using recycled pellets or fibers will have different properties than the original plastic. In addition, there is a limit to the number of times plastics can be recycled and reformed resulting in waste production. (Hein et al., 2014; Brunning, 2018)

#### Links to Enhanced Learning

To read more about how plastics are recycled, see this infographic from Chemical & Engineering News, Periodic graphics: How is plastic recycled? (https://cen.acs.org/environment/sustainability/ Periodic-graphics-plastic-recycled/96/i17).

Some of the major recycling processes include:

- Thermoplastic polymers can be melted and pelletized, but those of widely differing types must be treated separately to avoid incompatibility problems.
- Thermosetting polymers are usually shredded and used as filler material in recycled thermoplastic polymers.
- Thermal decomposition processes that can accommodate mixed kinds of plastics and render them into fuel oil, but the large inputs of energy they require have been a problem. Read more about Converting waste plastic bottles into jet fuel on the Chemistry World (https://www.chemistryworld.com/news/ converting-waste-plastic-bottles-into-jet-fuel-/3010455.article) website
- A small number of condensation polymers can be depolymerized so that the monomers can be recovered and re-used.
- A process to recycle scrap steel has been developed in which many kinds of plastic can be used as a carbon source.
- Mixed recycling of different plastics is possible. It does not require their separation and is called compatibilization. It requires use of special chemical bridging agents compatibilizers. Compatibilization can help to keep the quality of recycled material and to skip often expensive and inefficient preliminary scanning of waste plastics streams and their separation/purification.
- Re-use of rubber tires in the construction industry is one method to support the increasing reluctance of landfills to accept used tires.

#### Watch Plastic to Oil Fantastic on YouTube (5 mins) (https://youtu.be/R-Lg\_kvLaAM?)

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# 27.9 PLASTICS AND THE ENVIRONMENT

## Learning Objectives

By the end of this section, you will be able to:

- Describe the problems associated with plastics.
- Identify potential improvements in the formation and end-life of plastics.

Watch What really happens to the plastic you throw away – Emma Bryce on YouTube (4 mins) (https://youtu.be/\_6xlNyWPpB8?)

## **Problems with Plastics**

Due to their low cost, ease of manufacture, versatility, and imperviousness to water, plastics are used in a multitude of products of different scale, including paper clips and spacecraft. They have prevailed over traditional materials such as wood, stone, horn and bone, leather, metal, glass, and ceramic. However, there are numerous problems encountered with plastic use.

## Small-molecule release

Many kinds of polymers contain small molecules — either unreacted monomers, or substances specifically added (plasticizers, UV absorbers, flame retardants, etc.) to modify their properties. Many of these smaller molecules are able to diffuse through the material and be released into any liquid or air in contact with the plastic and eventually into the aquatic environment. Those that are used for building materials (in mobile homes, for example) can build up in closed environments and contribute to indoor air pollution.

#### Residual monomer

Formation of long polymer chains is a complicated and somewhat random process that is never perfectly

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stoichiometric. It is therefore not uncommon for some unreacted monomer to remain in the finished product. Some of these monomers, such as formaldehyde, styrene (from polystyrene, including polystyrene foam food take-out containers), vinyl chloride, and bisphenol-A (from polycarbonates) are known carcinogens. Although there is little evidence that the small quantities that diffuse into the air or leach out into fluids pose a quantifiable health risk, people are understandably reluctant to tolerate these exposures, and public policy is gradually beginning to regulate them.

For example, perfluorooctanoic acid (PFOA), the monomer from which Teflon is made, has been the subject of a 2004 lawsuit against a DuPont factory that contaminated groundwater. Small amounts of PFOA have been detected in gaseous emissions from hot fluorocarbon products.

#### Decomposition products

Most commonly used polymers are not readily biodegradable, particularly under the anaerobic conditions of most landfills. Also, what decomposition does occur will combine with rainwater to form leachates that can contaminate nearby streams and groundwater supplies. Partial photodecomposition, initiated by exposure to sunlight, is a more likely long-term fate for exposed plastics, resulting in tiny broken-up fragments. Many of these materials are less dense than seawater, and once they enter the oceans through coastal sewage outfalls or from marine vessel wastes, they tend to remain there indefinitely.

Open burning of polymeric materials containing chlorine (polyvinyl chloride, for example) is known to release compounds such as dioxins that persist in the environment. Incineration under the right conditions can effectively eliminate this hazard. Disposed products containing fluorocarbons (Teflon-coated ware, some personal-care, waterproofing and anti-stick materials) break down into perfluorooctane sulfonate which has been shown to damage aquatic animals.

#### Hazards to animals

There are two general types of hazards that polymers can introduce into the aquatic environment. One of these relates to the release of small molecules that act as hormone disrupters as described above. It is well established that small aquatic animals such as fish are being seriously affected by such substances in many rivers and estuarine systems, but details of the sources and identities of these molecules have not been identified. One confounding factor is the release of sewage water containing human birth-control drugs (which have a feminizing effect on sexual development) into many waterways.

The other hazard relates to pieces of plastic waste that aquatic animals mistake for food or become entangled in (Figure 27.9a.).



**Figure 27.9a.** A plastic bag (probably mistaken for a jellyfish, the sea turtle's only food) cannot be regurgitated and leads to intestinal blockage and slow death (left) remains of an albatross that mistook bits of plastic junk for food (right) (credit modifications of left: work by Coordinador copy, CC BY-SA 4.0; work by USFWS – Pacific Region (https://www.flickr.com/people/52133016@N08), CC BY-NC 2.0)

These dangers occur throughout the ocean but are greatly accentuated in regions known as gyres. These are regions of the ocean in which a combination of ocean currents drives permanent vortices that tend to collect and concentrate floating materials. The most notorious of these are the Great Pacific Gyres (Figure 27.9b.) that have accumulated astounding quantities of plastic waste.





# Plastics and Fire Hazards

The term fire (or flame)-retardant as applied to organic (carbon based) materials is intended to refer to reduced fire hazard, as all will burn under certain circumstances. Fabric flammability is an important textile issue, especially for stage drapery that will be used in a public space such as a school, theatre or special event venue. In the United States, federal regulations require that drapery fabrics used in such spaces be certified as flame or fire-retardant. For draperies and other fabrics used in public places, this is known as the NFPA 701 Test, which follows standards developed by the National Fire Protection Association (NFPA). Although all fabrics will burn, some are naturally more resistant to fire than others. Those that are more flammable can have their fire resistance drastically improved by treatment with fire-retardant chemicals. Inherently flame-retardant fabrics such as polyester are commonly used for flame retardant curtain fabrics.

The deaths in fiery crashes of race car drivers Fireball Roberts at Charlotte, and Eddie Sachs and Dave

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MacDonald at Indianapolis in 1964 led to the use of flame-resistant fabrics such as Nomex. Nomex and related aramid polymers are related to nylon, but have aromatic backbones, and hence are more rigid and more durable. Nomex is an example of a meta variant of the aramids. Kevlar is a para aramid. Unlike Kevlar, Nomex strands cannot align during filament polymerization and has less strength. However, it has excellent thermal, chemical, and radiation resistance for a polymer material.

A Nomex hood is a common piece of racing and firefighting equipment. It is placed on the head on top of a firefighter's face mask (Figure 27.9c.). The hood protects the portions of the head not covered by the helmet and face mask from the intense heat of the fire. Wildland firefighters wear Nomex shirts and trousers as part of their personal protective equipment during wildfire suppression activities. Racing car drivers wear driving suits constructed of Nomex and or other fire-retardant materials, along with Nomex gloves, long underwear, balaclavas, socks, helmet lining and shoes, to protect them in the event of a fire. Military pilots and aircrew wear flight suits made of over 92 percent Nomex to protect them from the possibility of cockpit fires and other mishaps. Recently, troops riding in ground vehicles have also begun wearing Nomex. Kevlar thread is often used to hold the fabric together at seams. Military tank drivers also typically use Nomex hoods as protection against fire.



Figure 27.9c. A firefighter in Toronto, Canada wears a Nomex hood in 2007. (Credit: Image by Sherurcij, ©)

## **Plasticizers and Pollution**

**Plasticizers** or dispersants are additives that increase the plasticity or decrease the viscosity of a material. These substances are compounded into certain types of plastics to render them more flexible by lowering the glass transition temperature. They accomplish this by taking up space between the polymer chains and acting as lubricants to enable the chains to more readily slip over each other (Figure 27.9d.). Many are small enough to be diffusible and a potential source of health problems.

#### 27.9 PLASTICS AND THE ENVIRONMENT | 663



**Figure 27.9d:** The blue lines represent the polymer chains; the red dots represent the plasticizer molecules. After the addition of the plasticizer the chains have more space, thus the material is more flexible. (Credit: Image by DaraDaraDara , CC BY-SA 4.0)

Polyvinyl chloride polymers are one of the most widely plasticized types, and the odours often associated with flexible vinyl materials such as garden hoses, waterbeds, cheap shower curtains, raincoats and upholstery are testament to their ability to migrate into the environment. The well-known "new car smell" is largely due to plasticizer release from upholstery and internal trim. According to 2014 data, the total global market for plasticizers was 8.4 million metric tonnes including 1.3 million metric tonnes in Europe.

Substantial concerns have been expressed over the safety of some plasticizers, especially because some low molecular weight ortho-phthalates have been classified as potential endocrine disruptors with some developmental toxicity reported. A common plasticizer identified in many common plastic containers was BPA or bisphenol-A (Figure 27.9f.). Due to health concerns, especially with young children, most plastic drinking cups and other kids items are listed as BPA-Free. Heating plastics containing plasticizers can encourage leaching of the chemicals. (Hein et al., 2014)



**Figure 27.9e.** Structure of bisphenol-A (BPA). (Credit: Image by Edgar181, PDM)

## **Plastics of the Future**

Current research is looking to the plastics of the future. Biodegradable plastics (Infographic 27.9a.) and different uses of plastic waste are regularly being reported. New sources of starting materials for plastics are being used (Infographic 27.9b.).



**Infographic 27.9a.** Chemistry of biodegradable plastics. Read more about "What's your biodegradable coffee cup made of – and how biodegradable is it? (https://www.compoundchem.com/2019/06/26/ biodegradable-plastics/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 27.9a [New tab] (#info27.9a).

# TURNING CARBON DIOXIDE INTO USEFUL PLASTICS

#### CARBON DIOXIDE: THE PROBLEM

Levels of carbon dioxide in our atmosphere have reached an alltime high. In addition to methods of reducing emissions, it's also important that we find ways of utilising the waste carbon dioxide present in our environment.

One way of doing this is to use catalysts to incorporate carbon dioxide in plastics which can then be used for a range of purposes.





Catalysts facilitate reaction between carbon dioxide and small reactive molecules called epoxides. This reaction makes a long chain of (n) repeat molecules called a copolymer, which are used to make plastic products. Captured waste carbon dioxide can be used as a starting point, and up to 40% of this used is incorporated into the final polymer.

The most prevalent application of the polymers produced by this method is incorporating them into polyurethanes.

Polyurethanes are a family of plastics which have a range of applications, including in memory foam mattresses, house insulation, the soles of trainers, and sports equipment including football coatings. Using this method makes production of these polyurethanes more environmentally sustainable.



# WHY DOES THIS RESEARCH MATTER?

By incorporating waste carbon dioxide already present in our environment into everyday plastics we can increase our environmental sustainability and decrease our dependency on fossil fuels.

Based on research and materials provided by Econic Technologies: Catalysts for Polymerisation



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**Infographic 27.9b.** Turning carbon dioxide into useful plastics. Chemistry of biodegradable plastics. Read more about "RealTimeChem Week: Turning Carbon Dioxide into Useful Plastics (https://www.compoundchem.com/2016/11/04/rtcw-co2-plastics/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 27.9b [New tab].

#### Links to Enhanced Learning

To read more about new polymers and upcycling polymers, see these suggested articles:

- New family of polymers can be easily recycled and even upcycled | Research | Chemistry World [New tab] (https://www.chemistryworld.com/news/new-family-of-polymers-can-beeasily-recycled-and-even-upcycled/3010439.article)
- Plastic packaging waste upcycled into technical materials | Research | Chemistry World [New tab] (https://www.chemistryworld.com/news/plastic-packaging-waste-upcycled-into-technical-materials/3009702.article)
- Genetically engineered microbes convert waste plastic into vanillin | Research | Chemistry World [New tab] (https://www.chemistryworld.com/news/genetically-engineered-microbesconvert-waste-plastic-into-vanillin/4013767.article)
- Polyurethane foams given a new lease of life as high-performance 3D printing inks | Research | Chemistry World [New tab] (https://www.chemistryworld.com/news/ polyurethane-foams-given-a-new-lease-of-life-as-high-performance-3d-printing-inks/ 4018003.article)

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(http://www.scc.losrios.edu/chemistry/))

• Wikipedia

#### References cited in text

Hein, M., Pattison, S., Arena, S., & Best, L. R. (2014). *Introduction to General, Organic, and Biochemistry* (11th ed.). Wiley.

## CHAPTER 27 - SUMMARY

## 27.1 Polymerization

Polymers are giant molecules that consist of long chains of units called monomers connected by covalent bonds. Polymerization is the process of linking monomers together to form a polymer. Plastic is the general term for polymers made from synthetic materials. Several important biological polymers include proteins, starch, cellulose, DNA and RNA.

## 27.2 Classification of Polymers

Plastics are polymers that are capable of being molded or are pliable. If they harden permanently when heated, polymers are classified as thermosetting; if they can be heated again and reformed repeatedly, they're classified as thermoplastic (Lower & Ophardt, n.d.) Addition polymerization is when the monomer molecules bond to each other without the loss of any other atoms. Condensation polymerization requires that the monomers possess two or more kinds of functional groups that are able to react with each other in such a way that parts of these groups combine to form a small molecule (often H<sub>2</sub>O) which is eliminated from the two pieces.

## 27.3 Polyethylene

Polyethylene is the long chain polymer formed from ethylene (ethene) monomers. Polyethylene can be classified as HDPE, LDPE, and others based on how close the polymer chains pack together affecting its density.

## 27.4 Addition Polymerization

Addition polymerization is when the monomer molecules bond to each other without the loss of any other atoms. Examples of addition polymers include polyethylene, polypropylene, polystyrene, polyvinylchloride, polytetrafluoroethylene, etc. Many objects in daily use from packing, wrapping, and building materials include half of all polymers synthesized. Other uses include textiles, many electronic appliance casings, CD's, automobile parts, and many others are made from polymers.

## 27.5 Rubber and Other Elastomers

The many uses of natural rubber have led to development and manufacture of synthetic rubber. Sulfur vulcanization is a chemical process for converting natural rubber or related polymers into more durable materials by heating them with sulfur or other equivalent curatives or accelerators. Three examples of synthetic rubber used in various applications are polybutadiene, polychloroprene (Neoprene), and styrene-butadiene rubber (SBR).

## 27.6 Condensation Polymers

Condensation polymerization (also known as step-growth) requires that the monomers possess two or more kinds of functional groups that are able to react with each other in such a way that parts of these groups combine to form a small molecule (often H<sub>2</sub>O) which is eliminated from the two pieces. The now-empty bonding positions on the two monomers can then join together. Examples of natural condensation polymers include cellulose, starch, and polypeptide chains of proteins. Several synthetic condensation polymers discussed include nylon, Kevlar, polyester, Bakelite, Melamine, polycarbonates, polyurethanes. Synthetic condensation polymers have a wide array of household, industrial, commercial, and medical uses and applications.

## 27.7 Properties of Polymers

The physical properties of a polymer such as its strength and flexibility depend on chain length, side groups present, branching, and cross-linking. Synthetic polymers may consist of both crystalline (more ordered, crystal-like) and amorphous (less ordered) regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material. The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Polymers with crystalline regions are generally tougher (can be bent more without breaking) and more impact-resistant than totally amorphous polymers. Due to their chemical structure, nylon, polyester, and acrylic fibers have physical properties that are comparable or even superior to natural fibers Thus, many of these fibers have a variety of uses and have replaced natural fibers in various products.

## 27.8 Plastics and Recycling

Plastics are found everywhere due to its low cost, versatility, ease of use etc. Plastic polymers are classified into seven groups for recycling purposes.

## 27.9 Plastics and the Environment

Plastics pose a threat to the environment due to residual or degradation products that contribute to air and water pollution. Plastics hazards to animals and marine life as these living creatures mistake them for food. Scientists are researching for new opportunities with plastic waste and production.

For an overall summary of Polymer Chemistry, watch Polymer Chemistry: Crash Course Organic Chemistry #35 – YouTube (https://youtu.be/dXaBkrS1HaM?) (13 min).

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#### References

Lower, S., & Ophardt, C. (n.d.). 10.2: Polyethylene – From the Battle of Britain to Bread Bags In Map: Chemistry for Changing Times (Hill and McCreary). Libre Texts, CC BY-SA.

## CHAPTER 27 - REVIEW

## 27.1 Polymerization

- 1. Explain the difference between monomer and polymer. Provide an example of each.
- 2. What is meant by the term "natural polymer"? "synthetic polymer"? Provide an example of each.
- 3. Which of the following is not a common natural polymer? Check answer<sup>1</sup>
  - a. Cellulose
  - b. Starch
  - c. Polyethylene
  - d. DNA

## 27.2 Classification of Polymers

- 1. Explain the differences between thermosetting and thermoplastic polymers. Provide an example of each.
- 2. Explain the differences between addition and condensation polymers. Provide an example of each.
- 3. Why is the term plastic used to describe some but not all polymers?
- 4. Looking at a monomer, how could you predict if the polymer will be formed by addition polymerization or condensation polymerization? Give at least two reasons.
- 5. What is the main characteristic of a thermosetting polymer? Check answer<sup>2</sup>
  - a. It can be melted and reshaped multiple times.
  - b. It softens when heated and hardens when cooled.
  - c. It undergoes irreversible chemical cross-linking when heated.
  - d. It remains flexible at all temperatures.

## 27.3 Polyethylene

- 1. Why is polyethylene not a co-polymer? Check answer<sup>3</sup>
- 2. Explain the similarities and differences between HDPE and LDPE.

## 27.4 Addition Polymerization

1. Draw the structural formula of the addition polymer created by the following monomers: a) ethene, b)

1-chloro-2-butene, c) bromoethene

- 2. Which monomer is primarily used in the synthesis of polyvinyl chloride (PVC)? Check answer<sup>4</sup>
  - a. Ethylene
  - b. Propylene
  - c. Vinyl chloride
  - d. Acrylonitrile
- 3. Which polymer is commonly used in making non-stick cookware due to its low coefficient of friction?

#### Check answer<sup>5</sup>

- a. Polyethylene
- b. Polypropylene
- c. Polystyrene
- d. Polytetrafluoroethylene (PTFE)
- 4. Which polymer is commonly used in the production of disposable food containers and packaging materials? **Check answer**<sup>6</sup>
  - a. Polystyrene
  - b. Polyethylene terephthalate (PET)
  - c. Polyurethane
  - d. Polybutadiene

## 27.5 Rubber and Other Elastomers

- 1. What are some of the benefits of the vulcanization of rubber process?
- 2. What were some of the drivers and impacts of the discovery of rubber?
- 3. Why are there geometric isomers of some polymers and not others? What is special about those polymers that can have geometric isomers?

## 27.6 Condensation Polymers

- 1. Which synthetic polymer is used in the production of clothing and textiles? Check answer<sup>7</sup>
  - a. Polyethylene
  - b. Polypropylene
  - c. Polyester
  - d. Polyvinyl chloride (PVC)
- 2. What is the primary use of polyurethane foam in construction and manufacturing? **Check answer**<sup>8</sup>
  - a. Insulation
  - b. Transparent windows

- c. Structural support beams
- d. Electrical conductivity

## 27.7 Properties of Polymers

1. List the four factors that influence a polymer's physical properties. Describe how each affects the polymer.

## 27.8 Plastics and Recycling

- 1. Do polymers need to be reduced to their monomers for recycling? Why or why not?
- 2. Describe some of the challenges associated with recycling plastics.
- 3. Research the recycling process in your local municipality. What plastics are accepted? What are not? How are the plastics recycled?
- 4. Research what is required in a waste audit. Conduct a mini waste audit of your household focusing on recyclable materials. What can you summarize about your household's plastic usage?
- 5. What changes are coming to the recycling program in Canada/Ontario? Research will be required.
- 6. Do you think it is easier to recycle a thermosetting or thermoplastic polymer? Why?
- 7. You have a neighbour who insists on putting all plastic materials in the recycling bin. Explain to the neighbour why only certain plastics can be recycled.

## 27.9 Plastics and the Environment

- 1. What is the primary function of a plasticizer in polymer formulations? Check answer<sup>9</sup>
  - a. Increase the melting point of the polymer
  - b. Enhance the electrical conductivity of the polymer
  - c. Improve the polymer's mechanical strength
  - d. Increase the flexibility and ease of processing of the polymer
- 2. What is the primary environmental impact of plastic pollution in oceans? Check answer<sup>10</sup>
- 3. How does plastic pollution affect terrestrial ecosystems? Check answer<sup>11</sup>
- 4. What role does microplastic pollution play in environmental degradation? **Check answer**<sup>12</sup>
- 5. What is the long-term impact of plastic accumulation in landfills? **Check answer**<sup>13</sup>
- 6. How can reducing single-use plastics benefit the environment? Check answer<sup>14</sup>
- 7. What is the Pacific Garbage Patch, and what are its environmental consequences? **Check answer**<sup>15</sup>

## Overall Thinking

- 1. Pick an item that is made of a polymer. Do some research to find out which polymer it is made of. If possible, sketch a skeletal drawing of the polymer.
- 2. Some of the data provided about various polymers in this chapter is US based. Pick one of the polymers and research it's use and production in Canada. Are the numbers similar? Are their different legislations regarding its use?

## **Attribution & References**

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#### References

Hein, M., Pattison, S., Arena, S., & Best, L. R. (2014). *Introduction to General, Organic, and Biochemistry* (11th ed.). Wiley.

#### Notes

- 1. c) Polyethylene
- 2. c) It undergoes irreversible chemical cross-linking when heated.
- 3. It is formed from one monomer unit, ethylene (ethene). Co-polymers require two or more different monomer units.
- 4. c) Vinyl chloride
- 5. d) Polytetrafluoroethylene (PTFE)
- 6. a) Polystyrene
- 7. c) Polyester
- 8. a) Insulation
- 9. d) Increase the flexibility and ease of processing of the polymer
- 10. The primary environmental impact of plastic pollution in oceans is the harm it causes to marine life, including ingestion and entanglement of animals, leading to injury and death.
- 11. Plastic pollution affects terrestrial ecosystems by contaminating soil and water sources, disrupting habitats, and potentially harming land-based wildlife through ingestion and entanglement.
- 12. Microplastic pollution plays a significant role in environmental degradation as these tiny plastic particles can infiltrate ecosystems, enter the food chain, and potentially harm both aquatic and terrestrial organisms.
- 13. The long-term impact of plastic accumulation in landfills includes the release of harmful chemicals as plastics degrade, potential groundwater contamination, and the persistence of non-biodegradable plastics for hundreds of years.

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- 14. Reducing single-use plastics can benefit the environment by decreasing the production and disposal of plastic waste, reducing pollution in ecosystems, conserving resources, and mitigating the carbon footprint associated with plastic production.
- 15. The Pacific Garbage Patch is a large accumulation of marine debris, primarily consisting of plastics, in the North Pacific Ocean. Its environmental consequences include harm to marine life, the release of toxins, and the disruption of ocean ecosystems due to the presence of non-biodegradable plastic waste.

## CHAPTER 27 - INFOGRAPHIC DESCRIPTIONS

### Infographics used in Chapter 27

- 27.0a Sticky Science The Chemistry of Superglue
- 27.0b The Myriad Uses of Stronger Than Steel Kevlar
- 27.0c Life in plastic(s): The chemistry of a Barbie doll
- 27.4a Today in Chemistry History Teflon
- 27.4b A Guide to Common Household Plastics
- 27.5a What are the Olympics athletics tracks made of?
- 27.6a Chemistry History Carothers, Condensation Polymerisation, & Nylon
- 27.7a What are Lego bricks made of, and why is treading on them so painful?
- 27.9a What's your biodegradable coffee cup made of and how biodegradable is it?
- 27.9b RealTimeChem Week: Turning carbon dioxide into useful plastics

#### 27.0a Sticky Science – The Chemistry of Superglue

Superglue was accidentally discovered twice.

In 1942, cyanoacrylates discovered during WWII search for gun sight plastics, was discarded as it stuck to everything.

In 1951, cyanoacrylates are rediscovered during research looking for polymers for jet canopies.

Cyanoacrylates potential realized and developed into glue that eventually becomes available commercially in 1958.

The most commonly used cyanoacrylate in superglue is ethyl cyanoacrylates. Others can be used: methyl cyanoacrylate. Medical grade cyanoacrylates such as 2-octyl cyanoacrylate can be used to close wounds.

Read more about "Sticky Science – The Chemistry of Superglue [New tab] (https://www.compoundchem.com/ 2015/10/15/superglue/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

## 27.0b The Myriad Uses of Stronger Than Steel Kevlar

Kevlar (polyparaphenylene terephthalamide) was discovered in 1965 by Stephanie Kwolek.

Polyparaphenylene terephthalamide has a density of 1.44g/cm3, a tensile strength 5 times stronger then steel (qual weight basis). There are many varieties: Kevlar, Kevlar 29, Kevlar 49, Kevlar 149.

Kevlar is a polymer – a very long, chain-like molecule which is formed by the reaction of multiple smaller molecules called monomers. It has a high strength, the result of many strong intermolecular hydrogen bonds between the adjacent polymer molecules. Monomers: 1,4-Phenylene-Diamine and Terephthaloyl Chloride.

The uses of Kevlar:

- Mobile phones: used for back casings of some mobile phone.
- Ping pong paddles: added to paddles to increase bounce and reduce weigh.
- Formula 1 cards: used for the bodywork and petrol tanks.
- Body armour: used for helmets, face masks and ballistic vests.
- Automobile types: used as a reinforcement material for some car tires and brake pads.
- Protective gloves: Used in the manufacture of gloves designed to protect form cuts and heat.
- Bicycle tires: Used as inner lining to prevent punctures.
- Fighter jets: used in manufacture of panels and wings.
- Fireproof clothing: Kevlar offers protection from high temperatures useful for firefighters.

#### Read more about "The Myriad Uses of Stronger Than Steel Kevlar [New tab] (https://www.compoundchem.com/2014/06/22/kevlar/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

### 27.0c Life in plastic(s): The chemistry of a Barbie doll

The head is made of polyvinyl chloride (PVC) mixed with plasticized to make it more flexible. The hair is usually made of polyvinylidene dichloride (PVDC) and other polymers including nylon and polypropylene.

Historically, Barbie doll arms were made of PVC, but today Barbie's arms are made of ethylene-vinyl acetate, which is soft and flexible.

The torso of early versions of Barbie was made out of PVC and in the mid-1960s to mid-1970s it was low density polyethylene (LDPE). Today, the torso is made of acrylonitrile butadiene styrene (ABS) – the same as Lego bricks.

The legs are made of PVC, with bend-leg armatures made of polypropylene. *Read more about "Life in plastic(s): The chemistry of a Barbie doll [New tab] (https://www.compoundchem.com/2023/08/18/barbie/)" by Andy Brunning / Compound Interest, CC BY-NC-ND* 

# 27.4a Today in Chemistry History – 4th February – Patent Issued for Teflon (1941)

Teflon is the brand name for polytetrafluoroethene (PTFE). It's a white, waxy substance, and was actually created by accident by Roy Plunkett in 1938. During research on new refrigerants, the tetrafluoroethene Plunkett was using was accidentally polymerised.

Tetrafluoroethene, CF<sub>2</sub>=CF<sub>2</sub>; polytetrafluoroethene, (CF<sub>2</sub>CF<sub>2</sub>)<sub>n</sub>

Image of Teflon pan

**How does it work?** Teflon's non-stick properties are in part due to the strength of its carbon-fluorine bonds, which are chemically inert. Additionally, due to the fluorine atoms, the intermolecular forces between PTFE and other molecules are very weak.

**Is Teflon safe?** During appropriate use, Teflon does not reach the temperatures required for it to degrade. However, if the coating is overheated the polymer can begin breaking down, and the fumes produced can cause flu-like symptoms. At present, the long term effects of human exposure to these fumes are still largely unknown.

Melting Point: 327°C, Recommended Max Safe Use Temperature: 260°C.

Read more about "Chemistry History: Teflon & Non-Stick Pans [New tab] (https://www.compoundchem.com/ 2016/02/04/teflon/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

#### 27.4b A Guide to Common Household Plastics

Plastics are substances called polymers – these are long, chain-like molecules, formed from many smaller molecules. We use a number of different plastics in our day-to-day lives. This graphic looks at uses of the most frequently encountered, along with their chemical structures.

#### **Common Household Plastics**

Abbreviation	Name	Structure	Details
PE	Polyethene	(CH <sub>2</sub> CH <sub>2</sub> ) <sub>n</sub>	Polyethene is the most produced plastic, and comes in a number of different forms, including high density polyethene (HDPE) and low density polyethene (LDPE). It is used in plastic bags, bottles, plastic films, piping, and toys. It is not biodegradable.
РР	Polypropene	(CH <sub>2</sub> CHCH <sub>3</sub> ) <sub>n</sub>	Polypropene is particularly resistant to heat, physical damage, and corrosion. As a consequence, it is commonly used in food containers, carpets and rugs, ropes, plastic furniture, and piping. It's also used to make items for medical or laboratory uses.
PVC	Polyvinylchloride	(CH <sub>2</sub> CHCl) <sub>n</sub>	PVC comes in both rigid and flexible forms. In its rigid form, it can be used for window and door frames, piping, and bank cards. By adding plasticisers, a more flexible form can be obtained, which is used in electric cable insulation, and as a rubber substitute.
PET	Polyethylene terephthalate	(OCOC <sub>6</sub> H <sub>4</sub> COOCH <sub>2</sub> CH <sub>2</sub> ) <sub>n</sub>	PET is a lightweight polymer, and comes in forms of varying rigidity. It's commonly used for plastic drink bottles, and also for clothing fibres (where it's often referred to generally as 'polyester'). Additionally, it's used in ready meal packing and tapes.
PS	Polystyrene	(CH <sub>2</sub> CHC <sub>6</sub> H <sub>5</sub> ) <sub>n</sub>	Polystyrene is one of the most widely used plastics. It's used in its solid form to produce plastic cutlery, CD cases, and disposable razors, whilst as a foam it's used in packing materials, building insulation, and foam containers for food and drink.
PTFE	Polytetrafluoroethene	(CF <sub>2</sub> CF <sub>2</sub> ) <sub>n</sub>	PTFE's well-known brand name is Teflon. It's a very unreactive polymer, and is used in non-stick coatings on cookware. Gore-tex fabrics also contain PTFE-based fibres. It also has applications as a lubricant, and as insulation for electric wires and cables.

Abbreviation	Name	Structure	Details
РА	Nylon (polyamide)	(NH(CH <sub>2</sub> ) <sub>6</sub> NHCO(CH <sub>2</sub> ) <sub>4</sub> CO) <sub>n</sub>	Nylon actually refers to a family of polymers; nylon 6,6 is shown here. It was originally intended as a synthetic silk replacement, for military applications such as parachutes. Today, it is used in clothing, guitar strings and fishing lines.
PU	Polyurethane	(RNHCOOROCONH) <sub>n</sub>	Polyurethanes are also a family of polymers; the R group in the structure above varies. Their uses include foam seating, for both furniture and cars, non-latex condoms, shoe soles, football coatings, skateboard and roller-blade wheels, and some varnishes.

Read more about "A Guide to Common Household Plastics [New tab] (https://www.compoundchem.com/2015/ 04/30/plastics/)" by Andy Brunning / Compound Interest, CC BY-NC-ND,

#### 27.5a What are the Olympics athletics tracks made of?

The 2020 Olympics use a specially designed track surface made from rubber (elastomeric polymer), which returns to its original shape when it's deformed. Other types of running track bind rubber particles with a polyurethane polymer over an asphalt base, and these track surfaces are commonly used for school and community tracks.

Top layer is embossed surface: The texture of the track surface improves slip resistance and traction, while the honeycomb layer of the bottom layers also aids shock absorption. Non-directional tessellation helps water drain from the surface and enhances grip.

Second layer is vulcanised rubber: Vulcanisation (treatment of rubber with sulfur) increases rubber's rigidity by forming crosslinks between rubber polymer chains.

Third layer is rubber granules embedded in the layers form bonds with the vulcanised rubber matrix, improving elasticity and shock absorption.

Bottom later are shaped like elongated honeycombs, which deform in three directions to help with shock absorptions and the air cells compress on impact allowing athletes to bounce off the surface.

Read more about "What are the Olympics athletics tracks made of? [New tab] (https://www.compoundchem.com/2021/08/07/athletics-track/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

# 27.6a Chemistry History – Carothers, Condensation Polymerisation, & Nylon

Wallace was born 27 April 1896 and died 29 April 1937. Carothers invented nylon using condensation polymerization, he also had a hand in inventing neoprene. Nylon is a polyamide, a type of condensation polymer. Condensation polymerization is when many monomers (smaller molecules) join together to make a polymer, with a small molecule, often water, being lost. A general scheme for making polyamides is shown.

Nylon 6,6 is made using monomers (hexanedioic acid and 1,6-Dianinohexane). Carothers' group first created nylon using these monomers in 1935.

Read more about "Chemistry History – Carothers, Condensation Polymerisation, & Nylon [New tab] (https://www.compoundchem.com/2016/04/27/nylon/)" by Andy Brunning / Compound Interest, CC BY-NC-ND,

# 27.7a What are Lego bricks made of, and why is treading on them so painful?

Up until 1963, cellulose acetate was used to make Lego bricks/parts. Lefo bricks are now made of acrylonitrile butadiene styrene (ABS), which warps and fades less.

Lego is made by using ABS granuales and adding macrolex dyes for colour, and then heating it to 230 degrees Celsius (450 degree Fahrenheit). The melted plastic is then fed into molds. ABS is opaque, so a polycarbonate polymer has to be used for transparent Lego parts. For leaves, bushes and trees, Lego has recently started using polyethene derived from sugar cane. Tires and elastic materials are made from styrene butadiene styrene (SBS).

In 2014, more the 60 billion Lego pieces were made.

Read more about "What are Lego bricks made of, and why is treading on them so painful? [New tab] (https://www.compoundchem.com/2018/04/09/lego/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

# 27.9a What's your biodegradable coffee cup made of – and how biodegradable is it?

#### Common biopolymers:

- 1. Polyactic acid (PLA): Obtained from fermented plant starch from corn, cassava, sugar cane or sugar beet.
- 2. Polyhydroxyalkanoates (PHAs): Extracted from bacteria, which produce it via the fermentation of sugar or lipids.
- 3. Thermoplastic starches (TPS): Startches from plant materials are heated with water then mixed with

plasicisers or other polymers.

#### Everyday use of biopolymers:

- Biodegradable coffee cups are paper cups with PLA lining to make the paper waterproof.
- PLA has the second largest production volume of any biopolymer (behind TPS). It is also used in plastic films, bottles and food containers.
- PLA and TPS both find use in the manufacture of plastic cutlery that's biodegradable.
- TPS is also used in food waste bags and some magazine wrappers. PHAs have fewer uses, but have medical uses such as in surgical sutures.

#### Advantages and disadvantages:

- Use of bioplastics is increasing, but as of 2018 they still account for less then 1% of the global plastic market: 333 million tons of conventional plastics and 2.11 million tons of biodegradable and bioplastics.
- Compostable plastics need specific conditions to break down and take longer to do so in a landfill instead of being recycled, however they still break down faster then conventional plastics.
- Biodegradable plastics are more expensive than plastics derived from fossil fuels on weight basis and require land to grow raw materials, but the greenhouse gas emissions associated with their production are lower.

Read more about "What's your biodegradable coffee cup made of – and how biodegradable is it? [New tab] (https://www.compoundchem.com/2019/06/26/biodegradable-plastics/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

### 27.9b RealTimeChem Week: Turning Carbon Dioxide into Useful Plastics

Levels of carbon dioxide in our atmosphere have reach an all-time high. In addition to finding methods to reduce emissions it is important to utilize the waste carbon dioxide in our environment. One way is to use catalysts to incorporate carbon dioxide into plastics.

Catalysts facilitate reaction between carbon dioxide and small reactive molecules called epoxides. This reaction makes a long chain of (n) repeat molecules called a copolymer, which are used to make plastic products. Captured waste carbon dioxide can be used as a starting point and up to 40% of this used is incorporated into the final polymer.

Most prevalent application of polymers produced is incorporating them into polyurethanes. Polyurethanes

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are a family of plastics with a range of applications including: memory foam mattresses, house insulation, shoe soles, and sports equipment. Using this method of production is more environmentally sustainable.

By incorporating waste carbon dioxide already present in the environment into everyday plastics it increases environmental sustainability and decreases our dependency on fossil fuels.

Based on research materials provided by Econic Technologies: Catalysts for Polymerisation.

Read more about "RealTimeChem Week: Turning Carbon Dioxide into Useful Plastics [New tab] (https://www.compoundchem.com/2016/11/04/rtcw-co2-plastics/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

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