Learning Objectives

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

Addition polymerization and condensation polymerization are two modes of polymerization reactions in the formation of 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. Ring opening polymerization can occur without the loss of any small molecules. Whereas, in condensation polymerization (Section 10.5) two different monomers combine with the loss of a small molecule, usually water. Most polyesters and polyamides (nylon) are in this class of polymers.

*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:

![Addition/bond rearrangement reaction](image)

In order to make this happen, a chemically active molecule (called an *initiator*) 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 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 (*chain termination*) to bring the polymerization to a halt.

![Chain initiation, propagation, and termination](image)

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.

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**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. 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 uncolored, 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 propene:

![Chemical structure of propylene and polypropylene](image)

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**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$^3$. 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 polymerisation, the carbon–carbon π bond of the vinyl group is broken and a new carbon–carbon σ bond is formed, attaching to the carbon of another styrene monomer to the chain.
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** (/ˌpɒlvɪznəl ˈkloʊrɪd/; colloquial: polyvinyl, vinyl; abbreviated: 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.

Polytetrafluorethylene (PTFE): The Nonstick Coating

**Polytetrafluoroethylene (PTFE)** is a synthetic fluoropolymer of tetrafluoroethylene that has numerous applications. The best-known brand name of PTFE-based formulas is Teflon (Figure \(\PageIndex{1}\)) Aldehydby Chemours. Chemours is a spin-off of DuPont, which 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.
Some common addition polymers are listed in Tables \(\PageIndex{1}\) and \(\PageIndex{2}\). 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.
<table>
<thead>
<tr>
<th>Monomer</th>
<th>Polymer</th>
<th>Polymer Name [Trade Name(s)]</th>
<th>Some Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_2=\text{CH}_2 )</td>
<td>(<del>\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2</del>)</td>
<td>polyethylene</td>
<td>plastic bags, bottles, toys, electrical insulation</td>
</tr>
<tr>
<td>( \text{CH}_2=\text{CHCH}_3 )</td>
<td>(<del>\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2</del>)</td>
<td>polypropylene</td>
<td>carpeting, bottles, luggage, exercise clothing</td>
</tr>
<tr>
<td>( \text{CH}_2=\text{C} \begin{array}{c} \text{C} \ \text{H} \ \text{H} \end{array} )</td>
<td>( \begin{array}{c} \text{C} \ \text{C} \ \text{H} \ \text{C} \ \text{C} \end{array} )</td>
<td>polystyrene</td>
<td>“take-out trays”, “packaging peanuts”, CD cases, foam-walled drink cups, and other thin-walled and moldable parts.</td>
</tr>
<tr>
<td>( \text{CH}_2=\text{CHCl} )</td>
<td>(<del>\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2</del>)</td>
<td>polyvinyl chloride</td>
<td>bags for intravenous solutions, pipes, tubing, floor</td>
</tr>
</tbody>
</table>
Monomer | Polymer | Polymer Name [Trade Name(s)] | Some Uses
--- | --- | --- | ---
CF₂=CF₂ | ~CF₂CF₂CF₂CF₂CF₂CF₂~ | polytetrafluoroethylene (Teflon) | Non-stick coating for cooking utensils, chemically-resistant specialty plastic parts, Gore-Tex

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<th>Trade Name(s)</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂C=CCl₂</td>
<td>polyvinylidene dichloride</td>
<td>Saran</td>
<td>Clinging food wrap</td>
</tr>
<tr>
<td>H₂C=CH(CN)</td>
<td>polyacrylonitrile</td>
<td>Orlon, Acrilan, Creslan</td>
<td>Fibers for textiles, carpets, upholstery</td>
</tr>
<tr>
<td>H₂C=CH(OCOCH₃)</td>
<td>polyvinyl acetate</td>
<td></td>
<td>Elmer’s glue - Silly Putty Demo</td>
</tr>
<tr>
<td>H₂C=CH(OH)</td>
<td>polyvinyl alcohol</td>
<td></td>
<td>Ghostbusters Demo</td>
</tr>
<tr>
<td>H₂C=C(CH₃)COOCH₃</td>
<td>polymethyl methacrylate</td>
<td>Plexiglass, Lucite</td>
<td>Stiff, clear, plastic sheets, blocks, tubing, and other shapes</td>
</tr>
<tr>
<td>H₂C=CH-C(CH₃)=CH₂</td>
<td>polysisoprene</td>
<td>natural or some synthetic rubber</td>
<td>applications similar to natural rubber</td>
</tr>
<tr>
<td>H₂C=CH-CH=CH₂</td>
<td>polybutadiene</td>
<td>polybutadiene synthetic rubber</td>
<td>select synthetic rubber applications</td>
</tr>
<tr>
<td>H₂C=CH-CCl=CH₂</td>
<td>polychloroprene</td>
<td>Neoprene</td>
<td>chemically-resistant rubber</td>
</tr>
</tbody>
</table>

**Processing Polymers**

**Molding** or **moulding** (see spelling differences) 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 metal mold then is softened by the heat and therefore forced to conform to the shape of the mold, as the mold closes. Once molding
is completed excess Flash may be removed. Typically, compression molding machines open along a vertical axis. **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 [Hayward] rather than open to the fill plunger resulting in higher dimensional tolerances and less environmental impact.\[^1\] Compared to injection molding, transfer molding uses higher pressures to uniformly fill the mold cavity. This allows thicker reinforcing fiber matrices to be more completely saturated by resin.\[^1\] Furthermore, unlike injection molding the transfer mold casting material may start the process as a solid. This can reduce equipment costs and time dependency. The transfer process may have a slower fill rate than an equivalent injection molding processes.

**Injection moulding** is a manufacturing process for producing parts by injecting molten material into a mould. Injection moulding 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. Material for the part is fed into a heated barrel, mixed (Using a helical shaped screw), and injected (Forced) into a mould cavity, where it cools and hardens to the configuration of the cavity.\[^1\]:240 After a product is designed, usually by an industrial designer or an engineer, moulds are made by a mould-maker (or toolmaker) from metal, usually either steel or aluminium, and precision-machined to form the features of the desired part. Injection moulding is widely used for manufacturing a variety of parts, from the smallest components to entire body panels of cars. Advances in 3D printing technology, using photopolymers which do not melt during the injection moulding of some lower temperature thermoplastics, can be used for some simple injection moulds.

**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. The two main advantages of this process over other manufacturing processes are its ability to create very complex cross-sections, and to work materials that are brittle, because the material only encounters compressive and shear stresses. It also forms parts with an excellent surface finish.\[^1\]

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.

Extrusion may be continuous (theoretically producing indefinitely long material) or semi-continuous (producing many pieces). The extrusion process can be done with the material hot or cold. Commonly extruded materials include metals, polymers, ceramics, concrete, modelling clay, and foodstuffs. The products of extrusion are generally called "extrudates".

Medical Uses of Polymers
An interesting use of polymers is the replacement of diseased, worn out, or missing parts in the body. For example, about 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.

**Figure \(\PageIndex{2}\):** 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.

Example \(\PageIndex{1}\))

Draw the polymer that results from the polymerization of tetrafluoroethylene.

![Polymer of tetrafluoroethylene](image)

**Solution**

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:

![Polymer structure](image)

**Exercise \(\PageIndex{1}\))

Draw the polymer that results from the polymerization of the following monomers:

a.

![Monomer a](image)

b.
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.

Summary

- 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.

Contributors and Attributions

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