

Chemical of the Week

POLYMERS

Polymers are substances whose molecules have high molar masses and are composed of a large number of repeating units. There are both naturally occurring and synthetic polymers. Among naturally occurring polymers are proteins, starches, cellulose, and latex. Synthetic polymers are produced commercially on a very large scale and have a wide range of properties and uses. The materials commonly called plastics are all synthetic polymers.

Polymers are formed by chemical reactions in which a large number of molecules called monomers are joined sequentially, forming a chain. In many polymers, only one monomer is used. In others, two or three different monomers may be combined. Polymers are classified by the characteristics of the reactions by which they are formed. If all atoms in the monomers are incorporated into the polymer, the polymer is called an *addition polymer*. If some of the atoms of the monomers are released into small molecules, such as water, the polymer is called a *condensation polymer*. Most addition polymers are made from monomers containing a double bond between carbon atoms. Such monomers are called olefins, and most commercial addition polymers are polyolefins. Condensation polymers are made from monomers that have two different groups of atoms which can join together to form, for example, ester or amide links. Polyesters are an important class of commercial polymers, as are polyamides (nylon).

POLYETHYLENE

Polyethylene is perhaps the simplest polymer, composed of chains of repeating $-\text{CH}_2-$ units. It is produced by the addition polymerization of ethylene, $\text{CH}_2=\text{CH}_2$ (ethene). The properties of polyethylene depend on the manner in which ethylene is polymerized. When catalyzed by organometallic compounds at moderate pressure (15 to 30 atm), the product is high density polyethylene, HDPE. Under these conditions, the polymer chains grow to very great length, and molar masses average many hundred thousands. HDPE is hard, tough, and resilient. Most HDPE is used in the manufacture of containers, such as milk bottles and laundry detergent jugs. When ethylene is polymerized at high pressure (1000–2000 atm), elevated temperatures (190–210°C), and catalyzed by peroxides, the product is low density polyethylene, LDPE. This form of polyethylene has molar masses of 20,000 to 40,000 grams. LDPE is relatively soft, and most of it is used in the production of plastic films, such as those used in sandwich bags.



HDPE



LDPE

POLYPROPYLENE

This polymer is produced by the addition polymerization of propylene, $\text{CH}_2=\text{CHCH}_3$ (propene). Its molecular structure is similar to that of polyethylene, but has a methyl group ($-\text{CH}_3$) on alternate carbon atoms of the chain. Its molar masses falls in the range 50,000 to 200,000 grams. Polypropylene (PP) is slightly more brittle than polyethylene, but softens at a temperature about 40°C higher. Polypropylene is used extensively in the automotive industry for interior trim, such as instrument panels, and in food packaging, such as yogurt containers. It is formed into fibers of very low absorbance and high stain resistance, used in clothing and home furnishings, especially carpeting.



PP

POLYSTYRENE

Styrene, $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$, polymerizes readily to form polystyrene (PS), a hard, highly transparent polymer. The molecular structure is similar to that of polypropylene, but with the methyl groups of polypropylene replaced by phenyl groups ($-\text{C}_6\text{H}_5$). A large portion of production goes into packaging. The thin, rigid, transparent containers in which fresh foods, such as salads, are packaged are made from polystyrene. Polystyrene is readily foamed or formed into beads. These foams and beads are excellent thermal insulators and are used to produce home insulation and containers for hot foods. Styrofoam is a trade name for foamed polystyrene. When rubber is dissolved in styrene before it is polymerized, the polystyrene produced is much more impact resistant. This type of polystyrene is used extensively in home appliances, such as the interior of refrigerators and air conditioner housing. [For more information about this polymer, see *Chemical Demonstrations: A Handbook for Teachers of Chemistry*, by Bassam Z. Shakhashiri, Volume 1 (1983), page 241.]



PS

POLYVINYL CHLORIDE

Polymerization of vinyl chloride, $\text{CH}_2=\text{CHCl}$ (chloroethene), produces a polymer similar to polyethylene, but having chlorine atoms at alternate carbon atoms on the chain. Polyvinyl chloride (PVC) is rigid and somewhat brittle. About two-thirds of the PVC produced annually is used in the manufacture of pipe. It is also used in the production of “vinyl” siding for houses and clear plastic bottles. When it is blended with a plasticizer such as a phthalate ester, PVC becomes pliable and is used to form flexible articles such as raincoats and shower curtains.



POLYETHYLENE TEREPHTHALATE

Polyethylene terephthalate (PET), or polyethylene terephthalic ester (PETE), is a condensation polymer produced from the monomers ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$, a dialcohol, and dimethyl terephthalate, $\text{CH}_3\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{CH}_3$, a diester. By the process of transesterification, these monomers form ester linkages between them, yielding a polyester. PETE fibers are manufactured under the trade names of Dacron and Fortrel. Pleats and creases can be permanently heat set in fabrics containing polyester fibers, so-called permanent press fabrics. PETE can also be formed into transparent sheets and castings. Mylar is a trade name for a PETE film. Transparent 2-liter carbonated beverage bottles are made from PETE. (The opaque base on some bottles is generally made of HDPE.) One form of PETE is the hardest known polymer and is used in eyeglass lenses.



POLYTETRAFLUOROETHYLENE

Teflon is a trade name of polytetrafluoroethylene, PTFE. It is formed by the addition polymerization of tetrafluoroethylene, $\text{CF}_2=\text{CF}_2$ (tetrafluoroethene). PTFE is distinguished by its complete resistance to attack by virtually all chemicals and by its slippery surface. It maintains its physical properties over a large temperature range, -270° to 385°C . These properties make it especially useful for components that must operate under harsh chemical conditions and at temperature extremes. Its most familiar household use is as a coating on cooking utensils.

POLYURETHANE

This important class of condensation polymers is formed by the polymerization of a diisocyanate (whose molecules contain two $-\text{NCO}$ groups) and a dialcohol (two $-\text{OH}$ groups). The polymer chain is linked by urethane groups ($-\text{O}-\text{CO}-\text{NH}-$). The $-\text{NH}-$ portion of the urethane group can react similarly to an $-\text{OH}$ group, producing cross-linking between polymer chains. Polyurethane is spun into elastic fibers, called spandex, and sold under the trade name Lycra. Polyurethane can also be foamed. Soft polyurethane foams are used in upholstery, and hard foams are used structurally in light aircraft wings and sail boards. The formation of some polyurethane (and polystyrene) foams exploits the exothermic nature of the polymerization reaction. A liquid with a low boiling point, called a blowing agent, is added to the monomers before the polymerization starts. As the polymerization proceeds, it releases enough heat to boil the liquid. The boiling liquid produces bubbles that create a foam. In the past, the most commonly used low-boiling liquids were chlorofluorocarbons. However, the damaging effect of chlorofluorocarbons on the stratospheric ozone layer has eliminated their use. Other low-boiling liquids have other disadvantages, such as flammability. Therefore, most polyurethane and polystyrene foams are manufactured by forcing a pressurized gas, such as nitrogen or carbon dioxide, into the polymerizing mixture. [For more information about this polymer, see *Ibid.*, Volume 1, page 216.]

POLYAMIDE

Polyamides are a group of condensation polymers commonly known as nylon. Nylon is made from two monomers, one a dichloride and the other a diamine. One particular nylon is made from 1,6-diaminohexane, $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$ and sebacyl chloride, $\text{ClCO}(\text{CH}_2)_8\text{COCl}$. When these polymerize, the resulting molecules contain repeating units of $-\text{NH}(\text{CH}_2)_6\text{NH}-\text{CO}(\text{CH}_2)_8\text{CO}-$. Molecules of HCl are released during the polymerization. This particular polymer is called nylon 6-10 because it contains alternating chains of 6 and 10 carbon atoms between nitrogen atoms. Nylon can be readily formed into fibers that are strong and long wearing, making them well suited for use in carpeting, upholstery fabric, tire cords, brushes, and turf for athletic fields. Nylon is also formed into rods, bars, and sheets that are easily formed and machined. In this form, nylon is used for gears and for automobile fuel tanks. [For more information about this polymer, see *Ibid.*, Volume 1, page 213.]

POLYACRYLAMIDE

Polyacrylamide is a condensation polymer with an unusual and useful property. The structure of polyacrylamide is similar to that of polyethylene, but having a hydrogen on every other carbon replaced by an amide group, $-\text{CONH}_2$. The molecule is composed of repeating $-\text{CH}_2-\text{CH}(\text{CONH}_2)-$ units. The amide groups allow for linking between polymer strands. The $-\text{CONH}_2$ group from one molecule can react with the same group of another molecule, forming a link between them with the structure $-\text{CONHCO}-$. This produces a network of polymer chains, rather like a tiny sponge. The free, unlinked amide groups, because they contain $-\text{NH}_2$ groups, can form hydrogen bonds with water. This gives the tiny cross linked sponges a great affinity for water. Polyacrylamide can absorb many times its mass in water. This property is useful in a variety of applications, such as in diapers and in potting soil. The polyacrylamide will release the absorbed water if a substance that interferes with hydrogen bonding is added. Ionic substances, such as salt, cause polyacrylamide to release its absorbed water. [For more information about this polymer, see *Ibid.*, Volume 3 (1989), page 368.]

Over the past few decades, the use of polymers in disposable consumer goods has grown tremendously. This growth is proving to be taxing on the waste disposal system, consuming a large fraction of available landfill space. Furthermore, the raw materials for these polymers are obtained from petroleum, a limited, non-renewable resource. To reduce the demand for landfill space and the consumption of limited petroleum reserves, the recycling of polymers has become a subject of concern. One of the problems faced in recycling polymers is the great variety of polymers in use. To help sort wastes by type of polymer, most disposable polymeric goods are labeled with a recycling code: three arrows around a number above the polymer's acronym. These are intended to help consumers separate the waste polymers according to type before disposing of them. (In the city of Madison, currently only type 1 (PETE) and type 2 (HDPE) polymers are being recycled – see below. These account for over 90% of all waste plastic containers. Other plastics comprise less than 1% of household waste.) The recycling of polymers is not a closed loop, where a material is reformed into new products repeatedly, such as is the case with aluminum. Most polymeric materials are recycled only once, and the product made of recycled polymer is discarded after use. To obtain the maximum benefit from recycled polymer, the products made from it generally are intended to have a relatively long useful life. Recycled polymers are used in such products as cafeteria trays, large plastic toys, impact absorbing highway pylons, and carpeting. Some recycled PETE is now used in 2-liter soft-drink containers. In general, products made from recycled polymers are more expensive than those made from virgin plastic. This is the case because current manufacturing facilities are geared to production from new materials. As more factories capable of using recycled plastics are constructed, the costs of using recycled polymers will decline. More such factories will be built soon only if we are willing to pay “up front” the costs of recycling (as higher prices of consumer goods), rather than delaying costs of disposal (in the form of increased taxes).



City of Madison Recycling Guidelines

The MadisonPride recycling program accepts the following plastic products for recycling:

- Plastic dairy and deli containers and their lids, Plastic clamshell and berry containers designated #1,
- Other plastic containers #1-7, and Plastic bags (except dark green or black).

Because there are no markets for these materials, the following plastics are not recycled (regardless of the number):

Styrofoam, Microwave dinner plates, Plastic wrap or cellophane

What Should I Do About Non-Recycled Plastic?

These plastics account for less than 10% of all plastic containers and make up less than 1% of household waste. Good markets for these materials do not exist at this time. Recycling this material would cost in excess of \$3,000 per ton, so it is not economical to do this at this time. Do not purchase products in a non-recyclable plastic containers if at all possible. Please look for products with alternative packages that come in containers marked with recycling symbols 1-7. Also, write to the manufactures who produce non-recyclable products and ask them to switch to recyclable containers.

Buy Soft Drink Containers With Recycled Content

Whenever you have a choice, you should buy soft drinks and drinking water in containers with recycled content. This helps the MadisonPride recycling program by insuring markets for the materials collected from your home for recycling. Currently, soft drink and water containers made of **glass** and **aluminum** have high percentages of recycled content. Unfortunately, plastic soft drink bottles have no recycled content. When plastic soda bottles are recycled, they are made into something other than bottles. This makes for weak markets and low prices for the used materials. Because plastic is so expensive to collect and process, poor markets make plastic costly to recycle.

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