General Chemistry (CH101): Chemistry around Us

Department of Chemistry

KAIST

Chapter 9
The World of Polymers and Plastics

- What are polymers?
- Where can you find polymers in your everyday life?
- How are polymers synthesized?
- What kinds of polymers can be recycled?
- How are polymers recycled?
- What are some environmental or health implications from our use of polymers?

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Reflect

Recycling Plastics

Watch the chapter opening video above, which shows how a soda bottle may be recycled into clothing. After watching that video, look at the plastic items around you and answer these questions:

a. Find three different items made from plastic with three different recycling symbols (a number within a triangle).

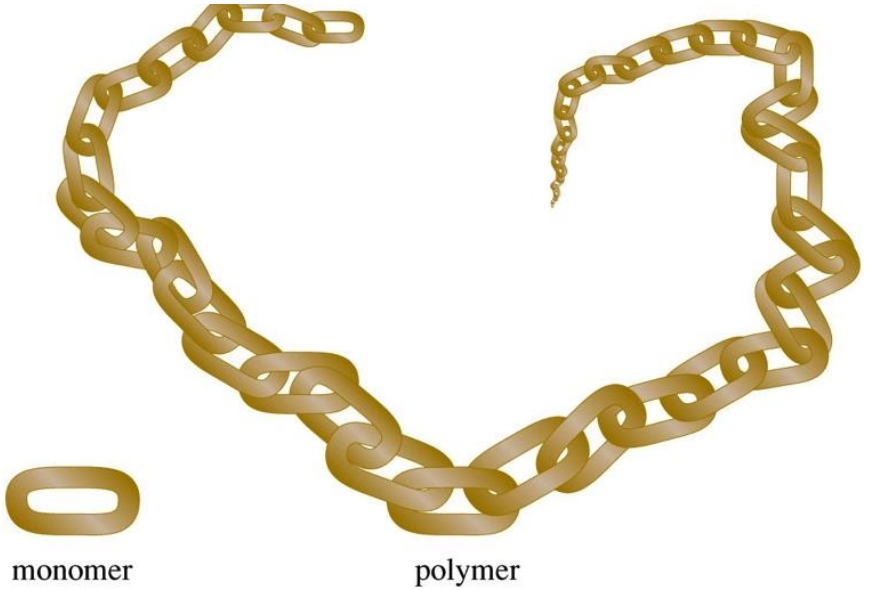
b. What do these symbols mean?

Chapter 9 video

Polymers and Monomers

Polymers are large molecules made up of long chains of atoms covalently bonded together.

Monomers (from *mono* meaning “one” and *meros* meaning “unit”) are the small molecules used to synthesize the polymeric chain, like a strand of paper clips.



Polymer Applications [1]

Your Turn 9.1 Tennis Anyone?

Examine the photo of a tennis player.

a. Choose three applications of polymers in the photo.

b. For the polymers you identified in **a**, describe some characteristics that are important for their intended use.

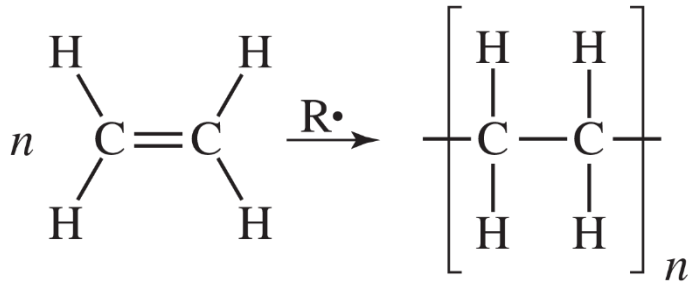
Polymers: Nothing New!

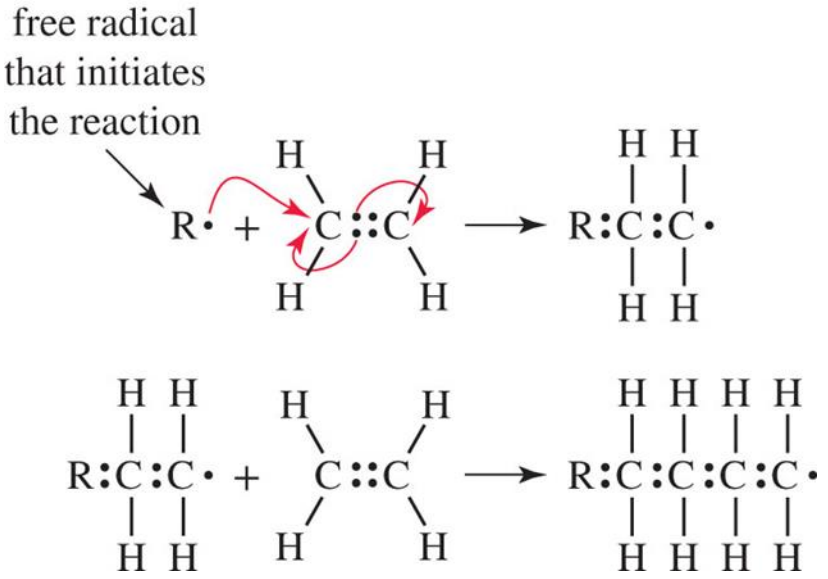
- Polymers have been with us since the beginning of time.
- **Natural polymers** include such things as cellulose, starch, tar and shellac, tortoise shell and horns, as well as tree saps that produce amber and latex.
- These polymers were processed with heat and pressure into useful articles like hair ornaments and jewelry.
- Natural polymers began to be chemically modified during the 1800s to produce many materials. The most famous of these were vulcanized rubber, cotton, and celluloid.

Hydrocarbons: The Backbone of Most Polymers

- Polymers are referred to as **macromolecules** because they involve thousands of atoms, and their molecular masses can reach over a million.
- Many common classes of polymers are composed of **hydrocarbons**. *C*arbon makes up the backbone of the molecule and hydrogen atoms are bonded to the carbon atoms.
- One example is **polyethylene**, the simplest polymer structure. Other examples of polymers that contain only carbon and hydrogen include polypropylene, polybutylene, and polystyrene.

Addition Polymerization: Polyethylene



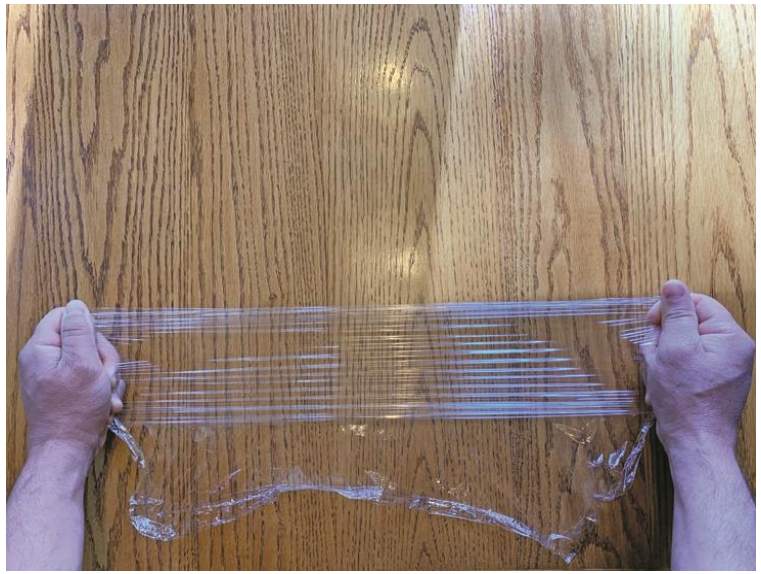


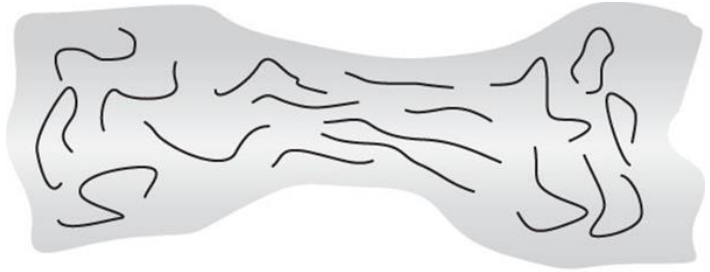
Polyethylene Uses

Your Turn 9.4 Polyethylene Hunt

Polyethylene containers, bags, and packaging materials are marked either as low-density (LDPE) or as high-density (HDPE). Using the recycling code as your guide, locate several items made from each. Do LDPE and HDPE differ in flexibility? Is one more translucent? Is one more often colored with a pigment than the other? Summarize your findings in a brief report.

Intermolecular Forces





- **Dispersion forces** (intermolecular forces) are attractions between molecules in the polymer that hold the material together.
- Stretching or “necking” a plastic bag illustrates the stress needed to overcome intermolecular forces between adjacent polymer chains.

Polymer Structure versus Properties

Your Turn 9.5 “Necking” Polyethylene

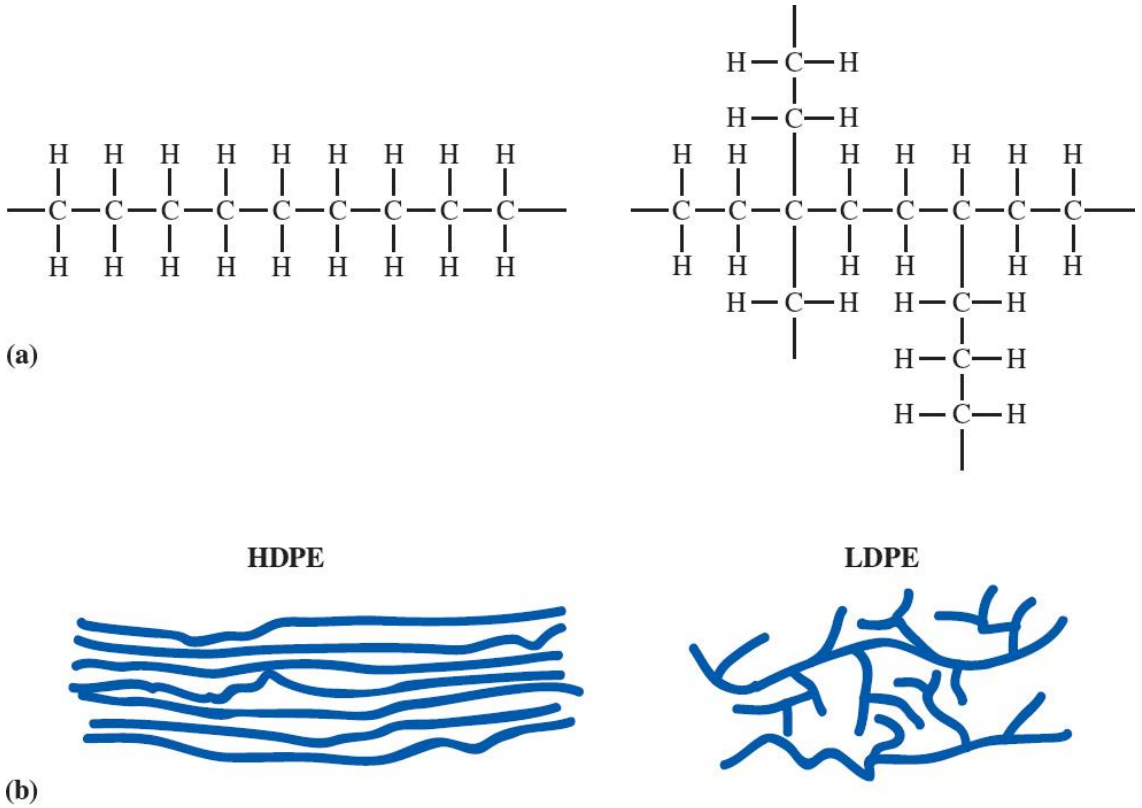
Necking permanently changes the properties of a piece of polyethylene.

a. Does necking affect the number of monomer units, *n,* in the average polymer?

b. Does necking affect the bonding between the monomer units within the polymer chain?

What Makes Rubber Rubbery?

Polymer Branching



- Branching alters the physical properties of a polymer such as polyethylene.
- High-density polyethylene (HDPE) has greater rigidity, strength, and melting point than low-density polyethylene (LDPE).
- Dispersion forces are stronger along polymer chains than among branches.

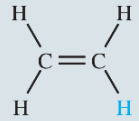
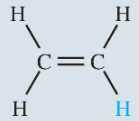
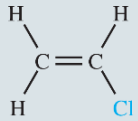
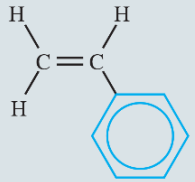
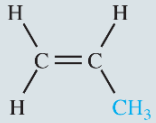
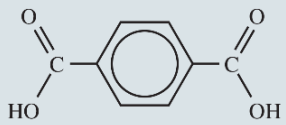
Synthetic Polymers: The ‘Big Six’ [1]

More than 60,000 synthetic polymers are known.

Six types account for about 75% of those used throughout the world:

- High-density polyethylene (HDPE): opaque milk, juice, detergent bottles.
- Low-density polyethylene (LDPE): bags, films, bubble wrap, wire insulation.
- Polyvinyl chloride (PVC): plumbing pipes, garden hoses, shower curtains.
- Polystyrene (PS): food wrap, foam cups, insulated containers, egg cartons.
- Polypropylene (PP): bottle caps, cream and margarine containers.
- Polyethylene terephthalate (PETE or PET): soft-drink bottles, carpet yarns.

All six of these varieties are thermoplastic polymers: they can be melted and reshaped over and over again.

Polymer Recycle Symbol	Monomer	Properties of Polymer	Uses of Polymer
Polyethylene  LDPE	Ethylene 	Translucent if not pigmented. Soft and flexible. Unreactive to acids and bases. Strong and tough.	Bags, films, sheets, bubble wrap, toys, wire insulation.
Polyethylene  HDPE	Ethylene 	Similar to LDPE. More rigid, tougher, slightly more dense.	Opaque milk, juice, detergent, and shampoo bottles. Buckets, crates, and fencing.
Polyvinyl chloride  PVC, or V	Vinyl chloride 	Variable. Rigid if not softened with a plasticizer. Clear and shiny, but often pigmented. Resistant to most chemicals, including oils, acids, and bases.	Rigid: Plumbing pipe, house siding, charge cards, hotel room keys. Softened: Garden hoses, waterproof boots, shower curtains, IV tubing.
Polystyrene  PS	Styrene 	Variable. "Crystal" form transparent, sparkling, somewhat brittle. "Expandable" form lightweight foam. Both forms rigid and degraded in many organic solvents.	"Crystal" form: Food wrap, CD cases, refrigerator shelves, transparent cups. "Expandable" form: Foam cups, insulated containers, food packaging trays, egg cartons, packaging peanuts.
Polypropylene  PP	Propylene 	Opaque, very tough, good weatherability. High melting point. Resistant to oils.	Bottle caps. Yogurt, cream, and margarine containers. Carpeting, casual furniture, luggage.
Polyethylene terephthalate  PETE, or PET	Ethylene glycol  Terephthalic acid 	Transparent, strong, shatter-resistant. Impervious to acids and atmospheric gases. Most costly of the six.	Soft-drink bottles, clear food containers, beverage glasses, fleece fabrics, carpet yarns, fiber-fill insulation.

Note: The structures of the first five monomers differ only by the atoms show in **blue**.

Thermoplastic Polymers

- All of the Big Six are **thermoplastic polymers** – they can be melted & reshaped with heat.
- In contrast to thermoplastics, some plastics are thermosetting. These solidify or “set” irreversibly with heat. Examples include rubber-soled footwear and antique Bakelite ovenware.

Shutterstock / kaczor58

Polymer Applications 2

Your Turn 9.10 Uses of the Big Six

Use Table 9.1 and other information provided about the Big Six to answer these questions.

a. Which polymer would not be suitable for margarine tubs because it softens with oil?

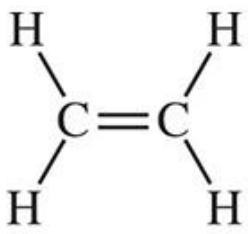
b. Which polymers are transparent? Which one is used in clear soft-drink bottles?

c. Which one is tough and used for bottle caps? Name another application in which toughness is important.

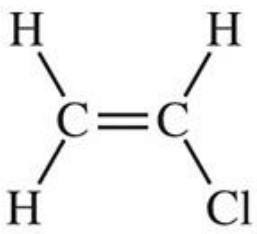
d. Which ones are listed as unreactive to acids and can serve as containers for acidic beverages, such as orange juice?

Monomer Similarities

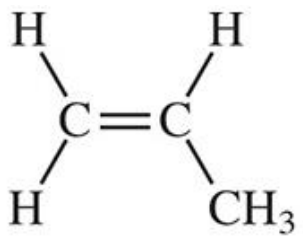
The molecular structures of all but PETE are very similar, varying by only a single functional group in their monomers:



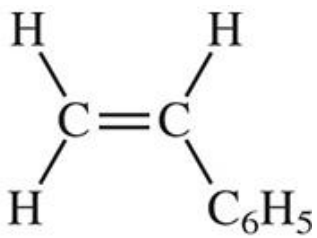
ethylene



vinyl chloride

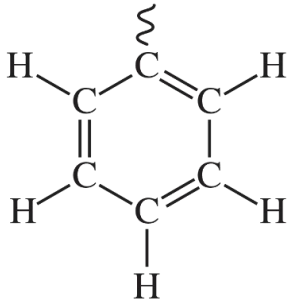


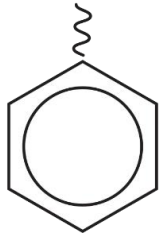
propylene

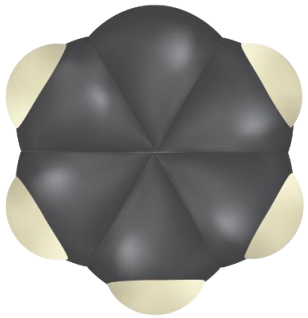


styrene

Phenyl Functional Group







Your Turn 9.12 Benzene and Phenyl

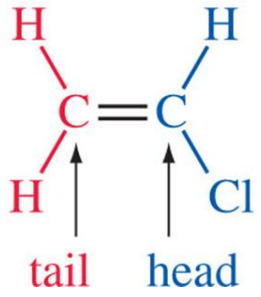
The difference between a phenyl group, —C_6H_5, and the compound benzene, C_6H_6, is simply one H atom.

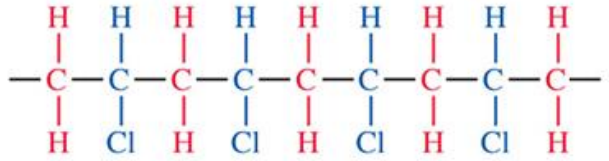
a. Both the phenyl group and benzene have two *resonance* structures. Draw them.

Hint: Resonance was introduced in Section 3.8.

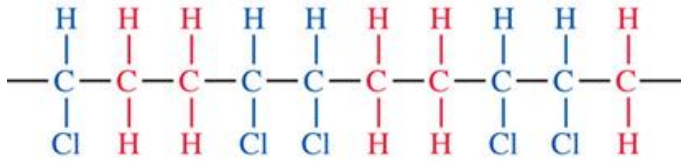
b. Given these resonance structures, why is the shorthand symbol of a circle within a hexagon a particularly good representation of both benzene and the phenyl group?

Polyvinyl Chloride (PVC)

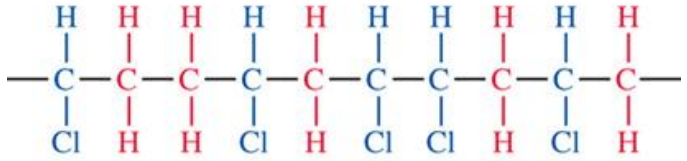




Head-to-tail, head-to-tail



Tail-to-tail, head-to-head

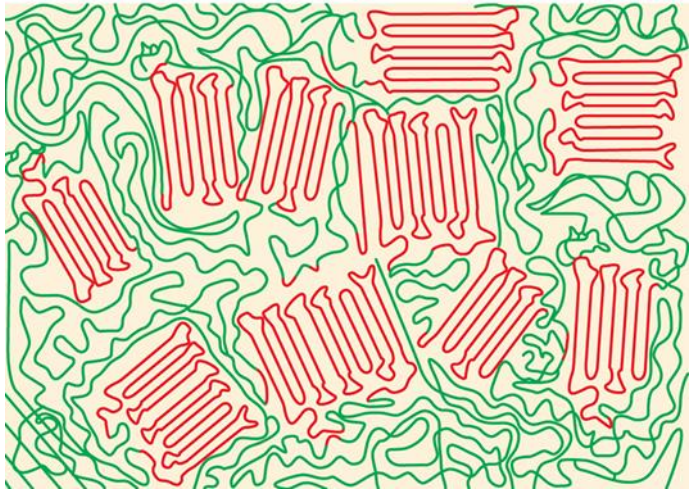


Random

- Vinyl chloride, propylene, and styrene monomers also undergo addition polymerization.
- Many different arrangements are possible when a polymer forms from polyvinyl chloride (PVC) monomers.
- How do these different arrangements affect the properties of the polymer?

Crystallinity

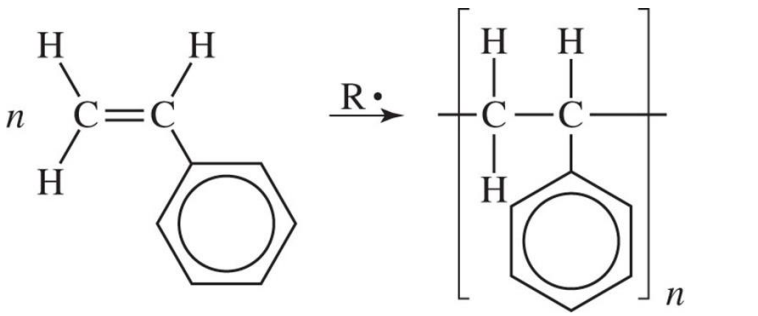
Head-to-tail: stiffest because molecules pack more easily to form crystalline regions.

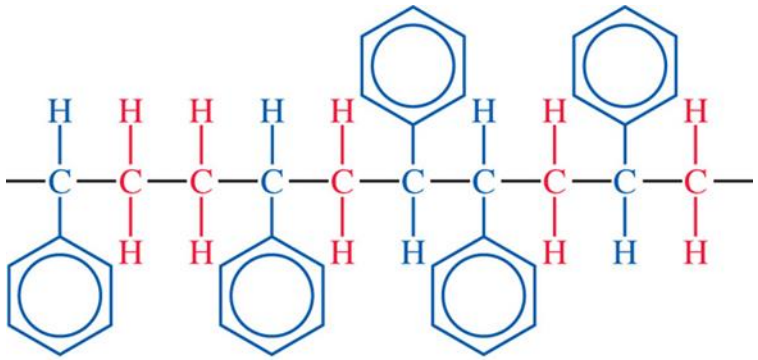


Head-to-head/tail-to-tail or random are less stiff; **plasticizers** can be used to further soften PVC.

- Polymers may have regions of **crystallinity**, wherein polymer molecules are arranged in a regular array.
- Other parts of the polymer will have **amorphous regions**, wherein polymer molecules are found in a random, disordered arrangement.
- Crystalline regions impart strength and abrasion resistance (found in high-density polyethylene and polyethylene).

Polystyrene (PS)





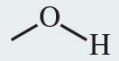
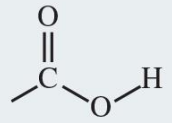
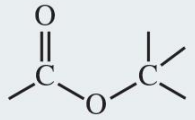
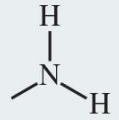
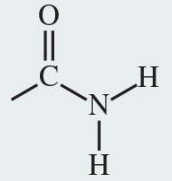
Random

- Polystyrene is a hard plastic with little flexibility.
- Like the other Big Six polymers, it melts when heated and casts well into molds.
- Transparent cases for DVDs and clear-plastic party glasses and plates are made from polystyrene.
- Expandable polystyrene (hot beverage cups, egg cartons, packing peanuts) contain a blowing agent, a gas that produces a foamed plastic.

Functional Groups

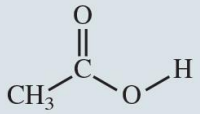
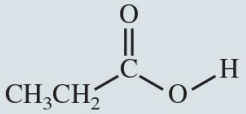
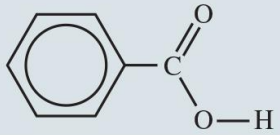
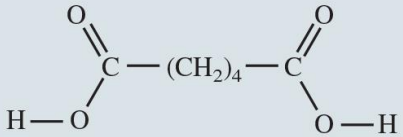
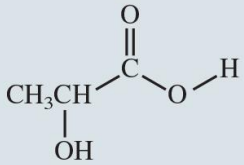
Functional groups are distinctive arrangements of groups of atoms that impart characteristic chemical properties to the molecules that contain them.

Table 9.2 Selected Functional Groups

Name	Chemical Formula	Structural Formula
hydroxyl (in alcohols)	–OH	
carboxylic acid	–COOH	
ester	–COOC–	
amine	$–NH_2$	
amide	$–CONH_2$	

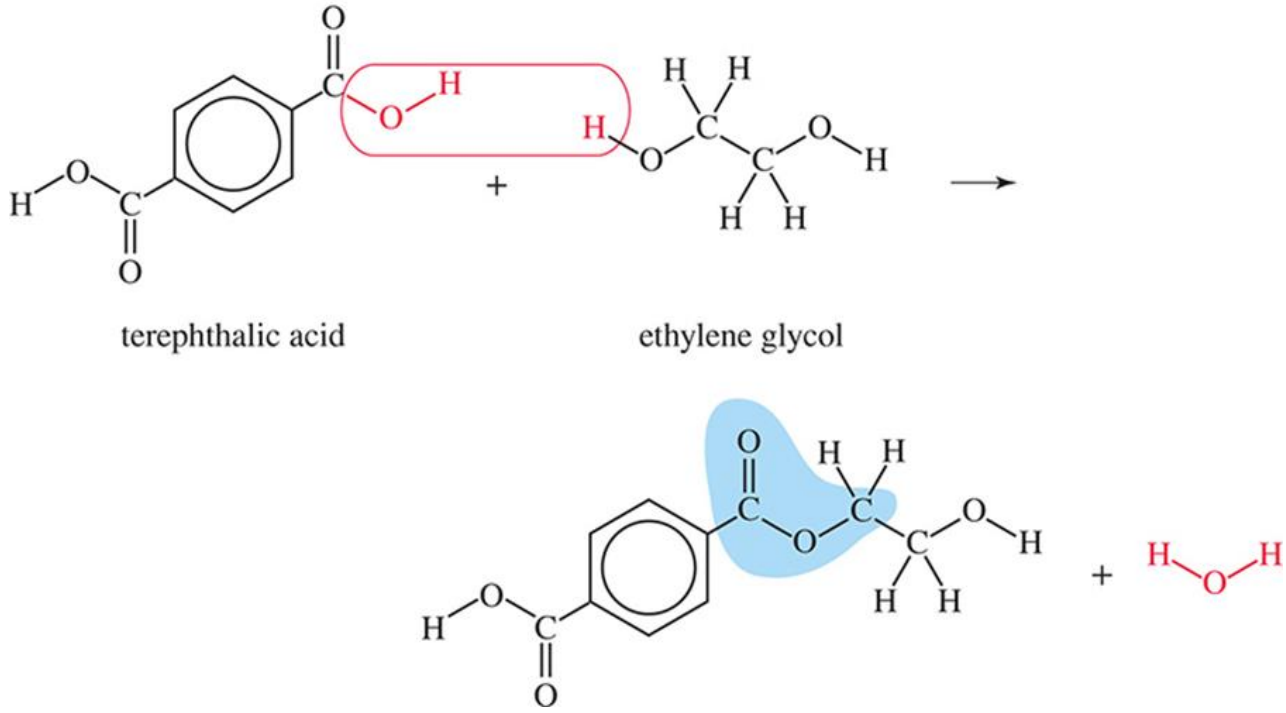
Carboxylic Acids

Table 9.3 Selected Carboxylic Acids

Name	Chemical Formula	Information
ethanoic acid		Naturally occurring in vinegar. Also called acetic acid.
propanoic acid		Naturally occurring in some cheeses, providing a “sharp” taste. Also called propionic acid.
benzoic acid		Another naturally occurring carboxylic acid. Used as a food preservative.
terephthalic acid		One of the monomers used to produce PET.
adipic acid		One of the monomers used to produce a type of nylon.
lactic acid		The monomer for polylactic acid (PLA), a bio-based polymer.

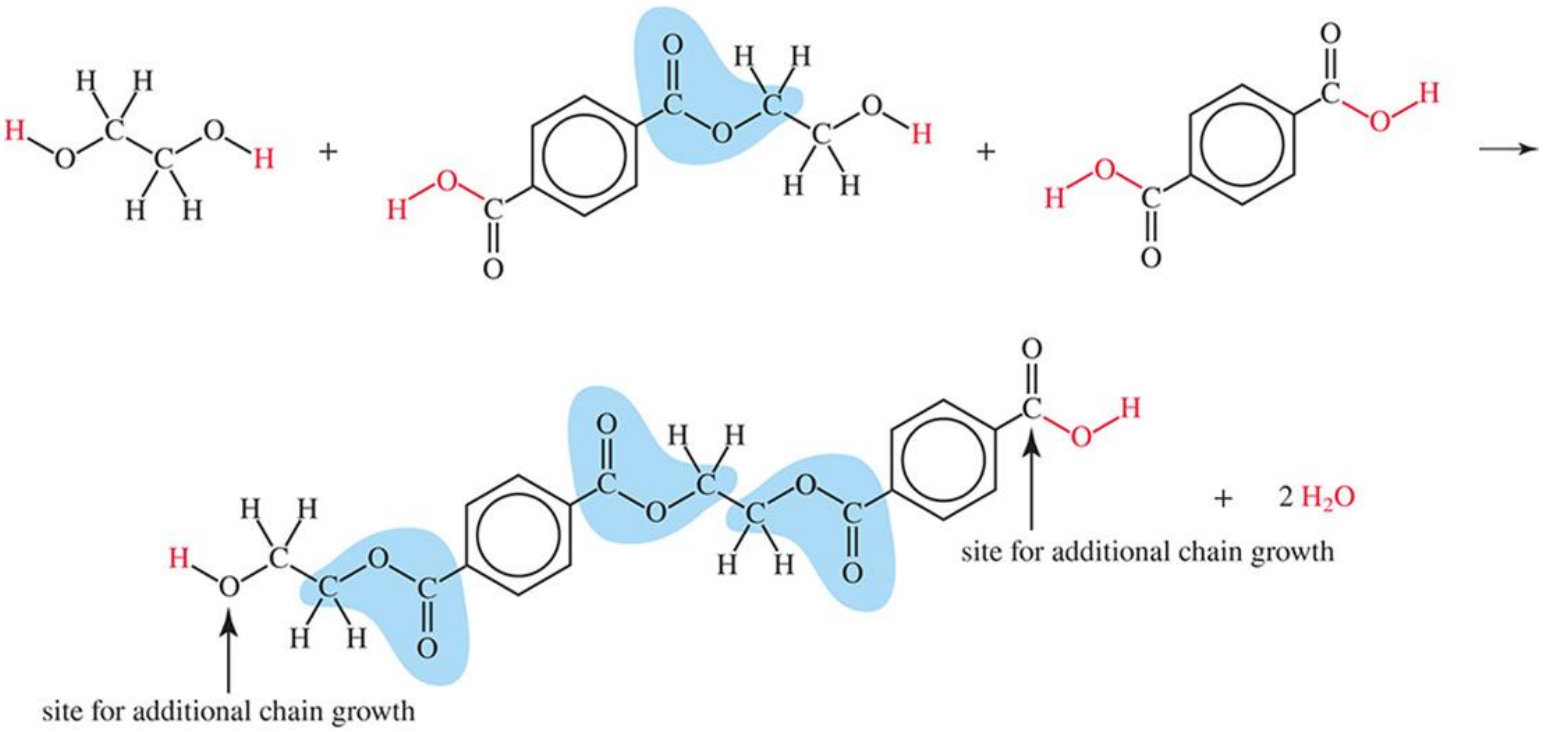
Condensation Polymerization

Instead of addition polymerization, some monomers crosslink together by eliminating a small molecule, such as water. Most natural polymers are formed by **condensation polymerization**, including starch, cellulose, wool, and proteins.



Polyesters [1]

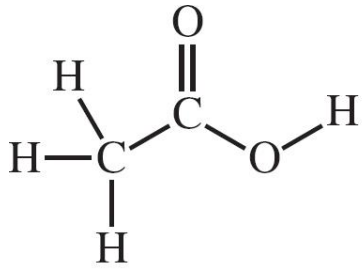
When an ester functional group connects the monomers, it is referred to as a **polyester** (used in clothing fabrics). One example is polyethylene terephthalate, PET:



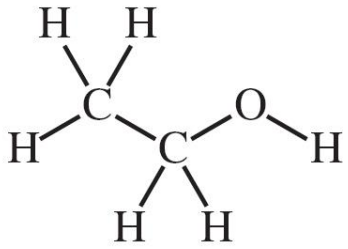
Polyesters 2

Your Turn 9.15 Esters and Polyesters

You have seen that terephthalic acid and ethylene glycol can react. Now consider ethanoic acid (acetic acid) and ethanol (ethyl alcohol):



ethanoic acid



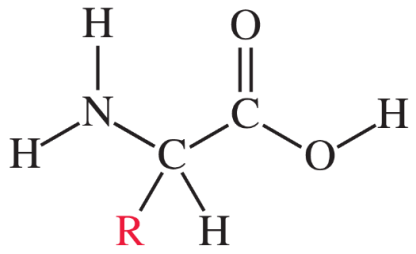
ethanol

a. Show how this carboxylic acid and alcohol can react to form an ester.

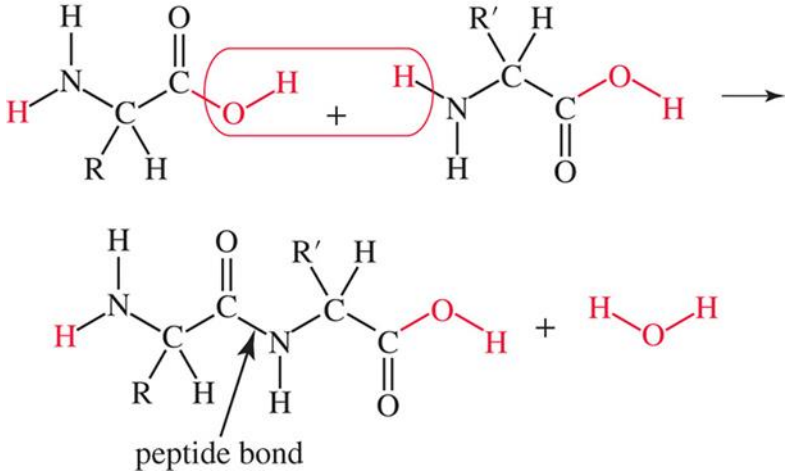
Hint: Remember a water molecule is formed as a product.

b. Could ethanoic acid and ethanol react to form a polyester? Explain your reasoning.

Proteins & Polyamides



The general structure of amino acids



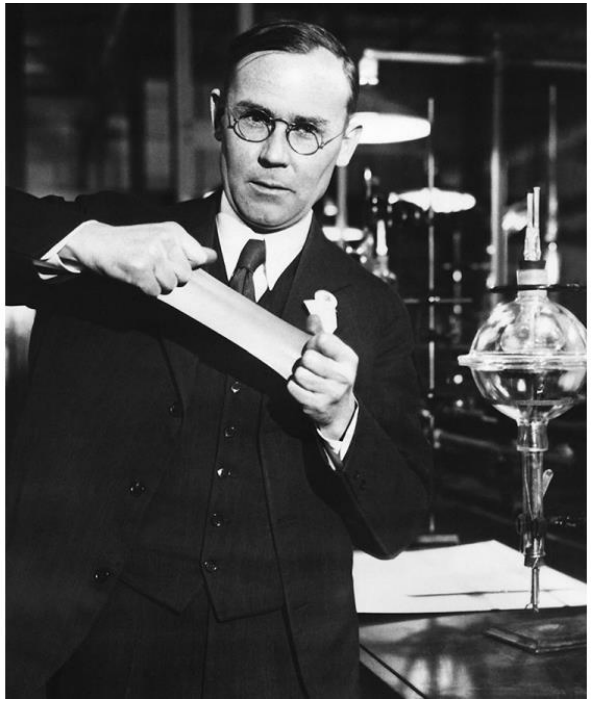
- Proteins are long chains of amino acids joined by condensation polymerization.
- **Peptide Bond**: covalent bond that forms between a carboxylic acid (–COOH) group of one amino acid and the amine ($–NH_2$) group of the next amino acid.

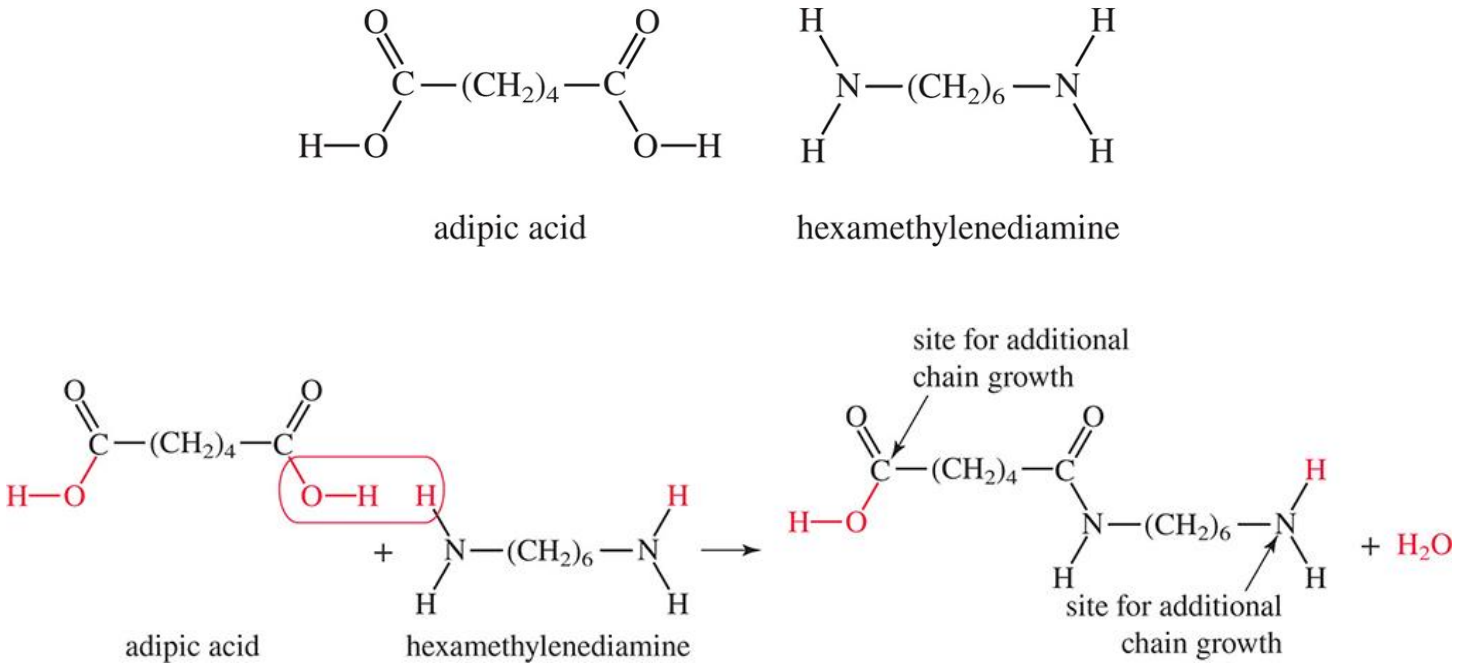
PET versus Proteins

- PET is a polyester whereas proteins are **polyamides**: condensation polymers that contain the amide functional group ($–CONH_2$).
- PET is formed from two monomers: ethylene glycol and terephthalic acid in a 1:1 ratio. In contrast, proteins can contain up to 20 different monomers (amino acids) in *any* ratio.
- In proteins, each amino acid has two *different* functional groups, $–NH_2$ and –COOH. In PET, the monomers have two *identical* functional groups, either –OH or –COOH.

Nylon

- Wallace Carothers at DuPont discovered Nylon by combining adipic acid with hexamethylenediamine.
- Nylon was the first substitute for silk and is the first biomimetic material-components for use in human applications that are developed using inspiration from nature.

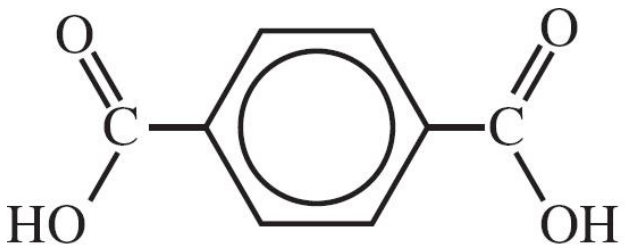




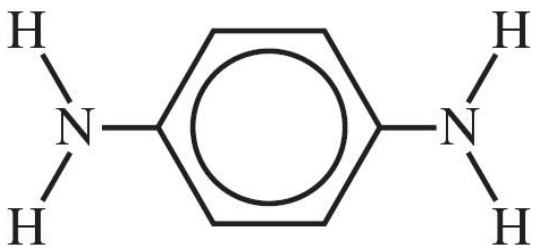
Can a Polyamide Stop Bullets?

Your Turn 9.17 Kevlar

Kevlar is a polyamide used in bulletproof vests and the cases of some cell phones. Like PET, one of the monomers is terephthalic acid. The other monomer, phenylenediamine, contains two amine functional groups:



terephthalic acid



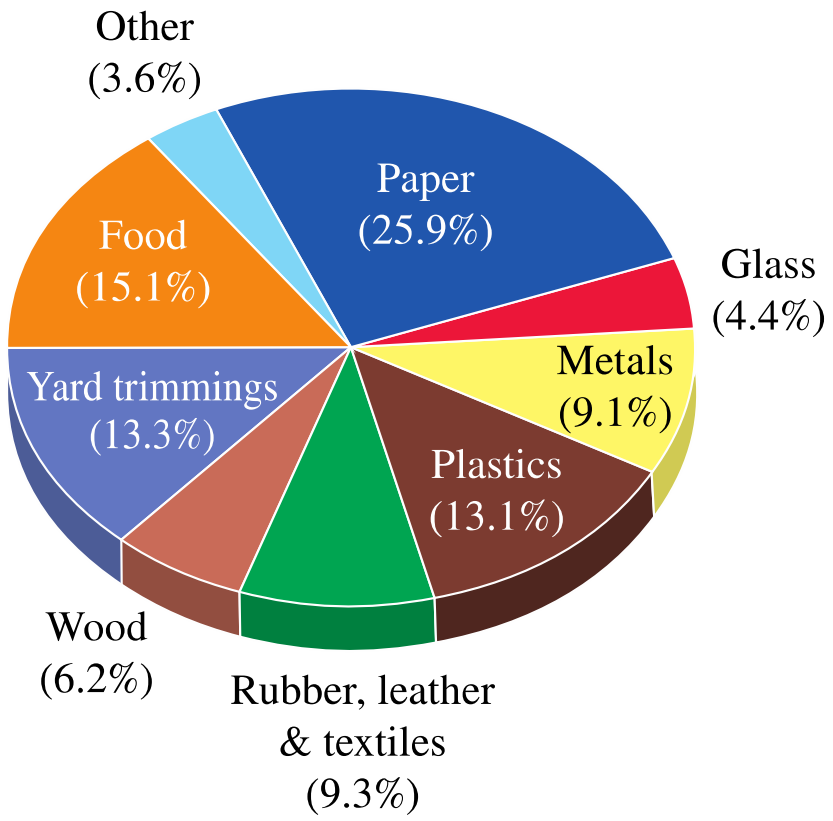
phenylenediamine

Draw a segment of a Kevlar molecule built from two of each of these monomers.

The Four Rs of Recycling

- **Reduce** the amount of materials used; for instance, use less plastic in the production of a bottle.
- **Reuse** materials; for instance, use you own bags at the grocery store.
- **Recycle** materials; that is, don’t throw beverage bottles away.
- **Recover** either the materials or the energy content from materials that cannot be recycled. For instance, burn unrecyclable plastics that contain a high-energy content.

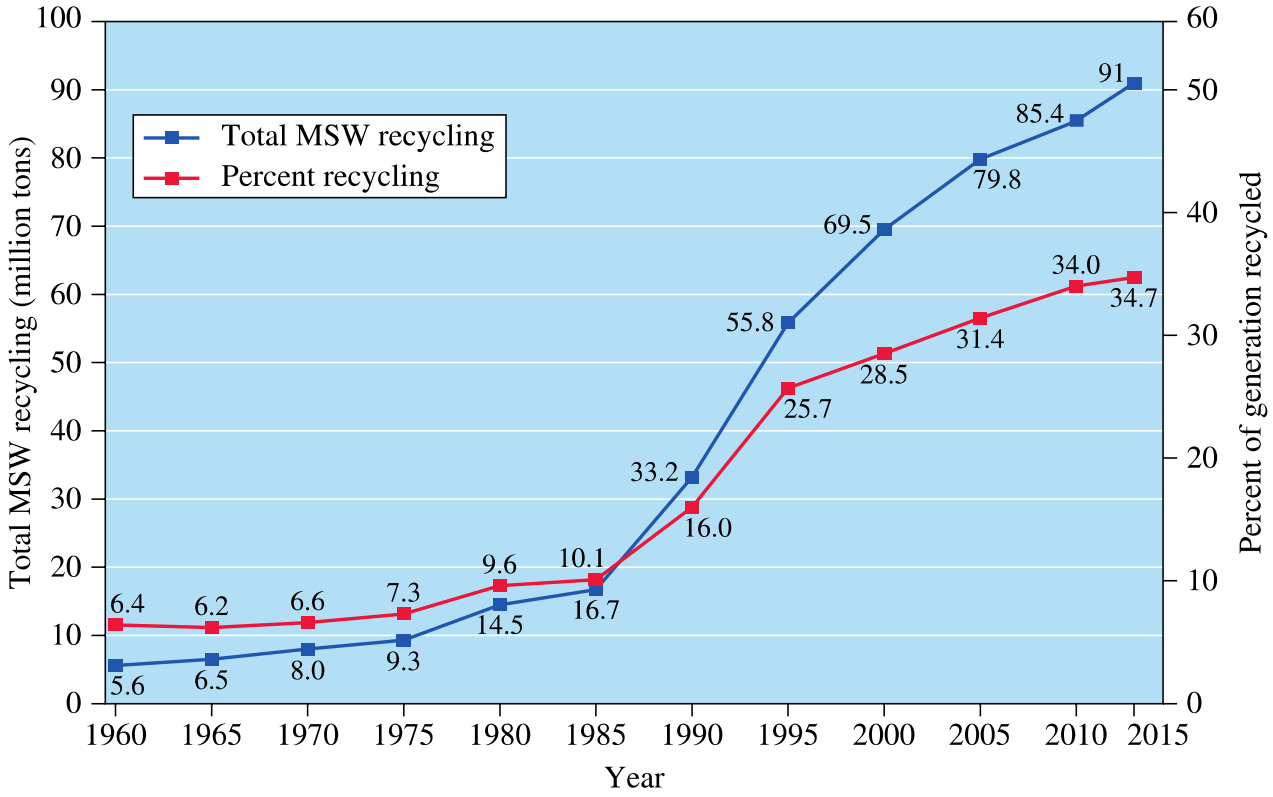
Composition of Municipal Solid Waste



- Municipal solid waste (MSW) includes all sources, such as waste from industry, agriculture, mining, and construction sites.
- In the U.S., MSW averages about 262 million tons per year.
- The majority of municipal waste is composed of paper, food, yard trimmings, and plastics.

Source: U.S. Environmental Protection Agency, Advancing Sustainable Materials Management: 2015 Fact Sheet, July 2018

Recycling Rate of Municipal Solid Waste



The overall rate of recycling and composting of total MSW (not just plastics) is currently around 35%.

Source: U.S. Environmental Protection Agency, Advancing Sustainable Materials Management: 2015 Fact Sheet, July 2018

Recycling Plastics

Table 9.4	Recycled Plastic Bottles in 2016	
Plastic	**Amount Recycled in 2016 (million pounds)**	**Recycling Rate**
PET	1753	28.4%
HDPE	1112	33.4%
PVC	1.4	4.3%
PP	36.6	20.2%
LDPE	2.6	3.7%

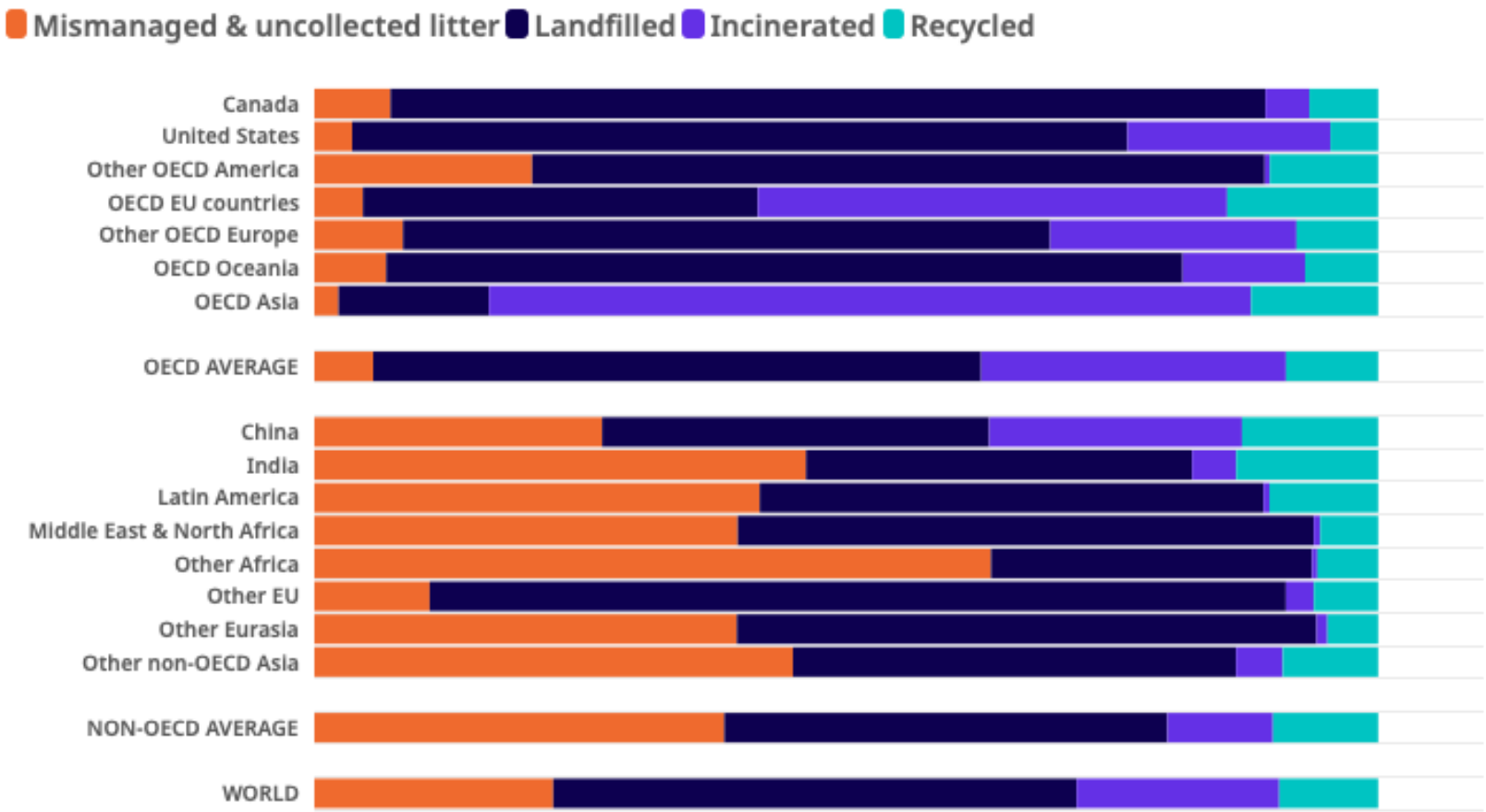
Source: American Chemistry Council, 2016, National Post-Consumer Plastic Bottle Recycling Report.

As of 2015, only 9.1% of plastic in the U.S. was recycled. Some polymers, such as those in plastic bottles, are heavily recycled, whereas others are almost never recycled.

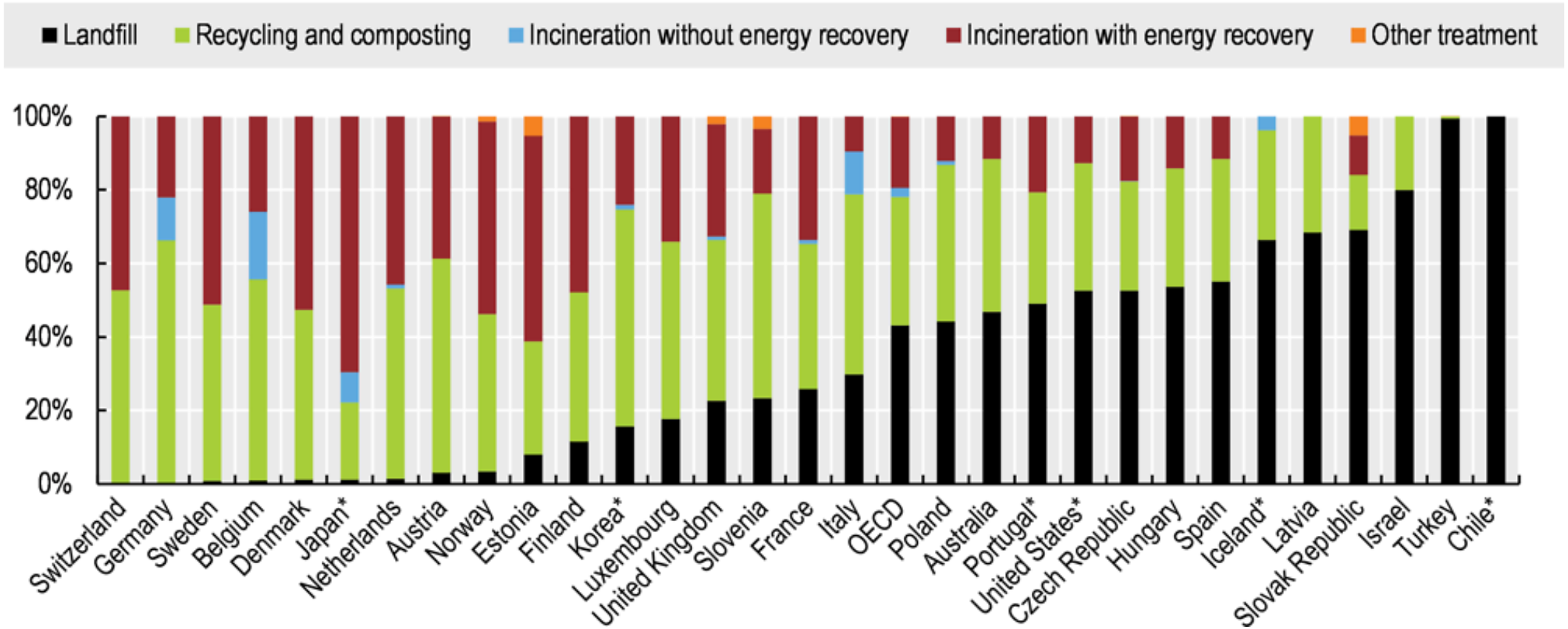
Source: American Chemistry Council, 2016, National Post-Consumer Plastic Bottle Recycling Report.

Globally, only 9% of plastic waste is recycled while 22% is mismanaged

Share of plastics treated by waste management category, after disposal of recycling residues and collected litter, 2019

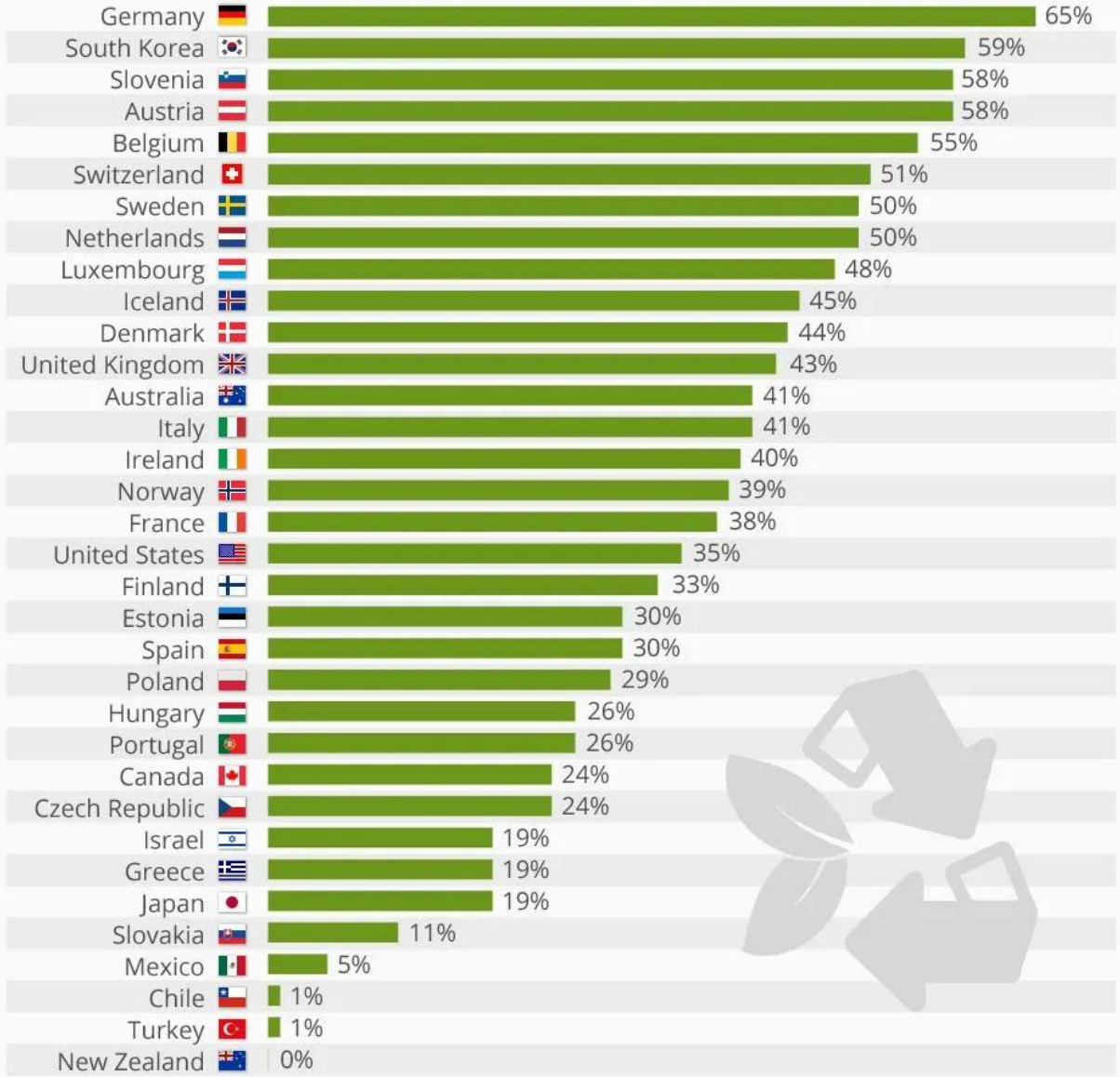


Treatment of MSW, 2015



The Countries Winning The Recycling Race

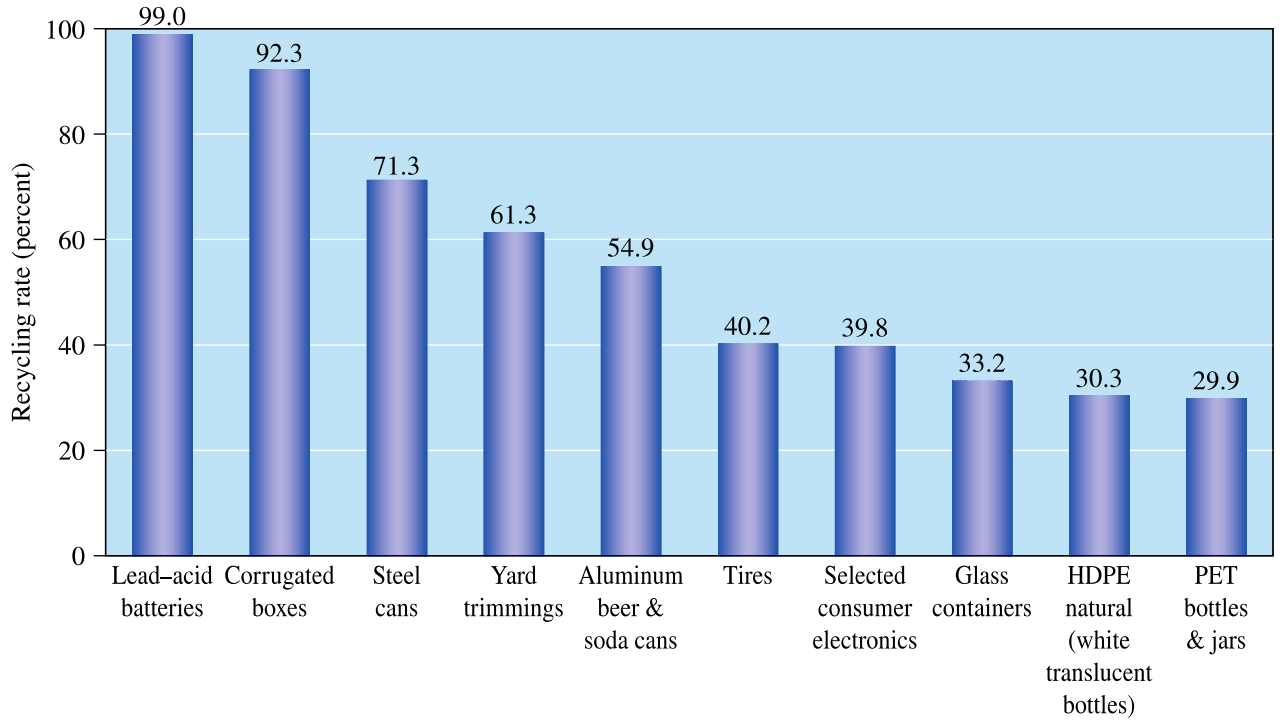
Recycled & composted waste as a share of total municipal waste in OECD countries (2013)



Source: OECD

Forbes statista

What Gets Recycled?

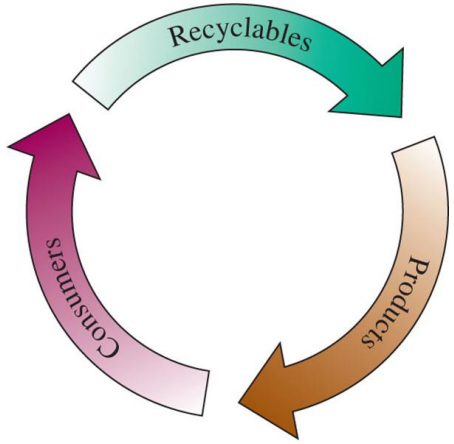


- Lead-acid batteries are almost always recycled, whereas polymers are much less frequently recycled.
- On average, only about 30% of plastic bottles are recycled – much less than aluminum and steel cans, yard trimmings, and newspapers/magazines.

How Plastic Recycling Actually Works

Cradle-to-Cradle Recycling

Recycling should involve a never-ending loop, from the use of one product that dovetails to another possible use through recycling.



Source: National Association for PET Container Resources

Your Turn 9.27 In a Store Near You

Unless people buy products made from recycled plastics, manufacturers will have little financial incentive to produce them. Find five recycled-content plastic items available for sale.

a. Identify the polymer(s) in each, and the % recycled content, if provided.

b. Comment on the consumer appeal of the item, including whether or not you would purchase it.

Separating Polymer Mixtures [1]

Your Turn 9.26 Float or Sink?

Here are density values for PET and for three other plastics likely to be found with it in a recycling bin:

Plastic	Density (g/cm^3)
PET	1.38 to 1.39
HDPE	0.95 to 0.97
PP	0.90 to 0.91
PVC	1.30 to 1.34

Separating Polymer Mixtures 2

When dropped into a liquid, a plastic will float or sink depending on the density of the liquid. Here are the densities for several liquids that do not degrade the four plastics above:

Liquid	Density (g/cm^3)
methanol	0.79
42% ethanol/water mixture	0.92
38% ethanol/water mixture	0.94
water	1.00
saturated solution of $MgCl_2$	1.34
saturated solution of $ZnCl_2$	2.01

Given a PET sample contaminated with HDPE, PP, and PVC, propose a way to separate the PET from the other three plastics. Assume that all density values were measured at the same temperature.

Plastics from Renewable Materials

Polymers originating from renewable sources such as wood, cotton, fibers, starch, or sugar are different from petroleum-based polymers:

- They are compostable; they are able to undergo biological decomposition to form a material that contains no toxic substances.
- Their synthesis involves fewer resources, results in less waste, and uses less energy.
- They do not contain chlorine or fluorine.
- Some polymers can be converted back into monomers and remade into virgin polymer.

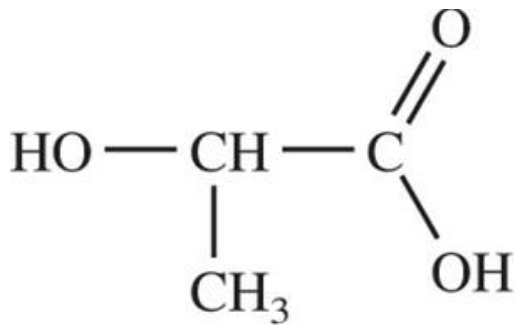
Recycled-content products: fabricated with materials that otherwise would have ended up in the waste stream.

Your Turn 9.25 Recyclable and Recycled

Give three examples of items that you might purchase and recycle. Also give three examples of recycled-content products. Can an item fall into both categories?

Polylactic Acid: A Common Renewable Polymer

- Polylactic acid (PLA) is a thermoelastic polyester, which has a similar look and feel to polyethylene terephthalate (PET).
- PLA softens at 140 °C, as compared to >250 °C for PET.
- Applications for PLA include clear shiny bottles, transparent food packaging, clothing fibers, plasticware, and coatings on paper cups and plates to make them water-resistant.
- Its monomer is lactic acid, which contains carboxylic acid and hydroxyl functional groups:



Degradation of PLA

© Pawarun/Getty

Check out this investigation to learn more about the degradation of PLA: www.acs.org/cic.

Your Turn 9.29 The Chemistry of PLA

We don’t show the chemical reaction for the formation of PLA from lactic acid because it does not proceed in a single step and is complicated. Even so, you should be able to write a chemical formula for PLA.

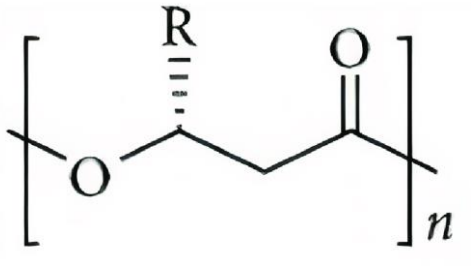
a. Circle and label the functional groups in the monomer, lactic acid.

b. When lactic acid polymerizes, explain how you know it is a condensation reaction.

c. What is the repeating unit in PLA?

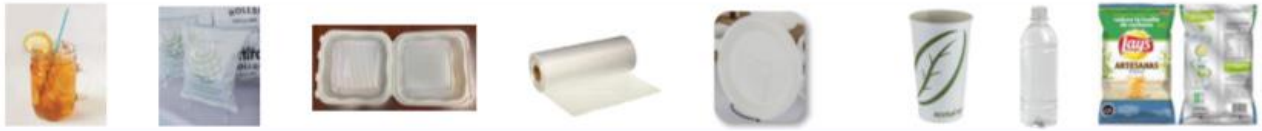
Is PLA for 3D printing really biodegradable? I've buried and drowned Benchy for 2 years to find out! (youtube.com)

PHA: Polyhydroxyalkanoates



[PHA Cycle Animation (youtube.com)]

Danimer Produces Bioplastics Based on PHA and PLA Technology

	PHA-Based Plastics	PLA-Based Plastics
Financials	2025E Revenue $403.4mm  nodax PHA	2025E Revenue $95.2mm 
Descriptions	▪ Proprietary bioplastic produced by bacteria that use canola and other plant-based oil feedstock for sources of energy ▪ Biodegrades in both anaerobic and aerobic environments and does not need heat and moisture to degrade	▪ Dextrose "sugar" based polymer derived from corn ▪ Industrially compostable ▪ Breaks down with heat and moisture added
Technology Offerings	▪ 100% bio-based technology that is recently fully commercialized under the proprietary Nodax® brand name ▪ Ability to convert PHA into articles for wide range of plastics and specialty applications ▪ Zero compromise on functionality	▪ Danimer purchases PLA and formulates into proprietary plastics using exclusive reactive extrusion technology ▪ Enhances application offerings via addition of additives ▪ Zero compromise on functionality
Select Customers	CPG Columbia Packaging Group; Genpak GenZero; Nestlé; PepsiCo; Ranir A Perrigo Company; Walmart; WinCup phade; UrthPact	
Product Applications		

Robust PHA Technology Portfolio of over 125 Patents across 20 Different Countries, Purchased from Procter & Gamble

A New Normal?

- One of the key components of sustainability is the concept of **shifting baselines** – the idea that what people expect as “normal” on our planet has changed over time.
- For instance, most beverages used to be bottled in glass. Now, they are in PET bottles and aluminum cans.

Your Turn 9.31 Glass or Plastic?

a. Even though selling milk in glass bottles may be coming back in style, plastic jugs or plastic-coated cartons are still the norm in most places. List two advantages and disadvantages of using glass bottles. Do the same for using plastic bottles.

b. Today, if not sold in aluminum cans, soft drinks are sold in plastic bottles and beer is sold in ones made of glass. Research and report on at least two reasons for the difference.

Does History Repeat Itself?

The properties of plastics that make them useful in the first place mean that plastics persist in landfills for many years. Does this sound familiar?

Your Turn 9.32 Lessons from Refrigerators Past

Chlorofluorocarbons, better known as CFCs, were once widely used in refrigerators, aerosol sprays, foams, and medical inhalers.

a. Why were CFCs phased out?

b. Some CFCs remain in the atmosphere for 100 years or more. Explain how this property of CFCs is connected to the fact that they have been phased out.

c. Name some properties that polymers such as HDPE, LDPE, PVC, and PS share with CFCs.

d. Unlike CFCs, it is highly unlikely that plastics will be phased out. Offer some reasons why.

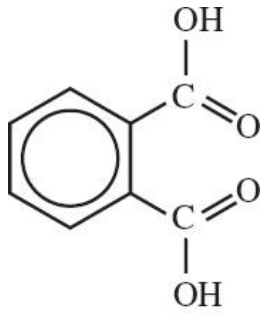
e. Some people believe that we cannot sustain our current use of plastics. Give evidence that either supports or contradicts this statement.

Harmful Polymer Additives [1]

Plasticizers are not chemically bonded to the plastic, but are mixed into the polymer when being fabricated to make the final product softer and more pliable. Over time, these polymer additives leach out into the environment. One controversial plasticizer is di-2-ethylhexyl phthalate (DEHP):

Your Turn 9.33 Meet DEHP

DEHP belongs to a common class of plasticizers called *phthalates* (THAL-ates). Phthalates are esters of phthalic (THAL-ic) acid, an isomer of terephthalic acid, one of the monomers used to synthesize PET.

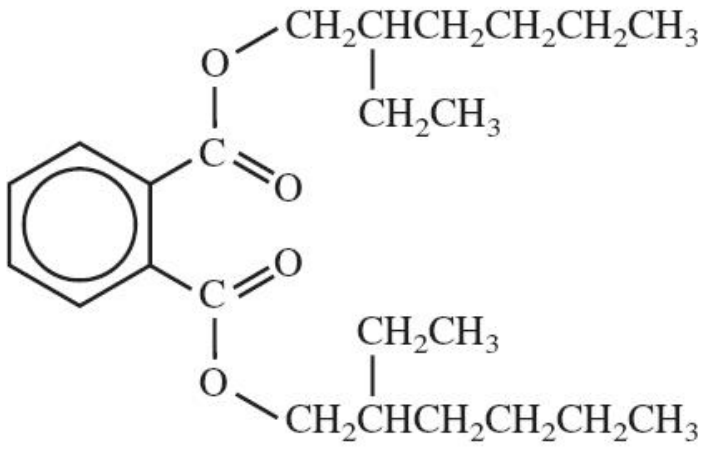


phthalic acid

Harmful Polymer Additives 2

a. Explain the meaning of the term ester.

b. Below is the structural formula for DEHP. Circle the two ester groups in this molecule.



DEHP

c. Draw a structural formula for the alcohol that reacted with terephthalic acid to form this ester.

The Precautionary Principle

- Phthalate additives are suspected endocrine disrupters, affecting the human hormone system, including those used for reproduction and sexual development.
- To date, no research has unequivocally proven that plastic additives such as DEHP or bisphenol A (BPA) cause harm to human health.
- However, DEHP and BPA have been banned from plastic bottles and infant pacifiers and childrens' toys. This is an application of the precautionary principle – the wisdom of acting, even in the absence of complete scientific data, before the adverse effects on human health or the environment become significant or irrevocable.

The Dangerous Chemicals In Your Plastic Packages (youtube.com)

Invisible Dangers

Your Turn 9.34 Group Activity: What are *Microplastics?*

Plastics represent the most prevalent variety of debris found in oceans and the Great Lakes. Although we typically think of plastic contaminants as discarded packaging material or plastic cups, there is another type that is much smaller in dimensions. Using the Internet as a resource, answer the following questions as a group:

a. What are “microplastics” and in which consumer products are these materials found?

b. How widespread are microplastic pollutants in marine environments worldwide?

c. What are some of the potential impacts posed to human health or marine life from exposure to microplastics?

d. What legislation has been initiated to reduce the harmful effects of microplastics? Have these actions resulted in any measurable improvements in the concentration of these marine pollutants, to date?

Example topics that you can delve into further...

1. Assess whether nuclear power plants are a viable alternative energy source, supporting your argument with scientific evidence.
2. Explore the health impacts of indoor radon exposure, identify its primary sources, and suggest methods to decrease its concentration.
3. Investigate if there are any materials that can serve as substitutes for silicon in photovoltaic cells.
4. Analyze the reasons behind the significant growth in wind power and its advantages compared to other energy sources.
5. Determine the more suitable location for wind power generation: offshore (sea) or mountainous areas.