

INTRODUCTION

- Advancement in technology is directly associated with the development of new materials
- History is often dated by the materials of most importance to the society, i.e., the Stone, Bronze, and Iron Ages
- The most important materials in the modern society are plastics, ceramics, and steel

HISTORY

Natural Macromolecules

- A living organism is a complex machine, most functions of which are performed by macromolecules.
- DNA, RNA, ribosomers, proteins, cellulose, starches, and a host of other biologically important substances are all macromolecules.
- From the very beginning of civilization, humans made technological use of natural macromolecules: leather, fur, wool, wood, cotton, flax, paper, natural rubber, etc.

Man-made (Synthetic) Macromolecules

- 1839 Elastic property improvement of natural rubber by vulcanization
- 1870 Commercialization of celluloid (75% cellulose nitrate + 25% camphor)
- 1892 Preparation of rayon textile fibers
- 1910 Phenol-formaldehyde resins - first fully-synthetic polymers
- 1920 Staudinger's hypothesis of "macromolecules"
- 1930 Firm establishment of the concept of polymers

Nobel Prizes for Polymer Science

- 1953 **H. Staudinger**
Introduction of the concept of polymers (but not colloids)
- 1963 **K. Ziegler and G. Natta**
Discovery of coordination polymerization catalysts and preparation of stereoregular polymers
- 1974 **P. J. Flory**
Theoretical and experimental contributions to fundamental principles of polymer science
- 1991 **G. de Gennes**
Successful mathematical treatment of phase transition phenomena of polymers, liquid crystals, and superconducting materials
- 2000 **A. J. Heeger, A. G. MacDiarmid, and H. Shirakawa**
Discovery and development of conductive polymers

Basic Definition and Nomenclature

Polymer: a substance composed of molecules which have long sequences of one or more species of atoms or groups of atoms linked to each other by primary, usually covalent, bonds.

Usually, a molecule is considered to be macromolecular when it exhibits properties typical of high molecular weight substances.

Macromolecules are formed by linking together **monomer** molecules through chemical reactions, the process by which this is achieved being known as **polymerization**.

Linear polymers may be represented by a chain with two ends.

Branched polymers have side chains, or branches, of significant length which are bonded to the main chain at branch points, and are characterized in terms of the number and size of the branches.

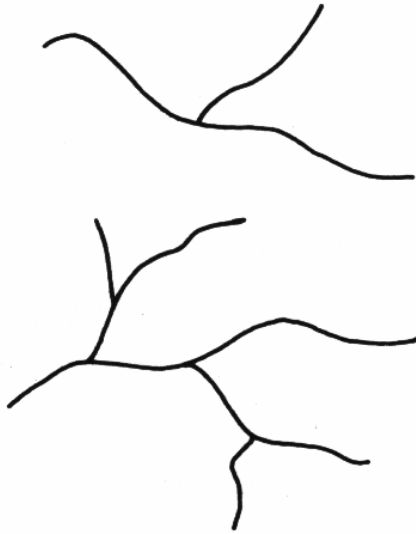
Polymers with well-controlled modes of branching:

comblike polymers, star polymers, dendrimers, *etc.*

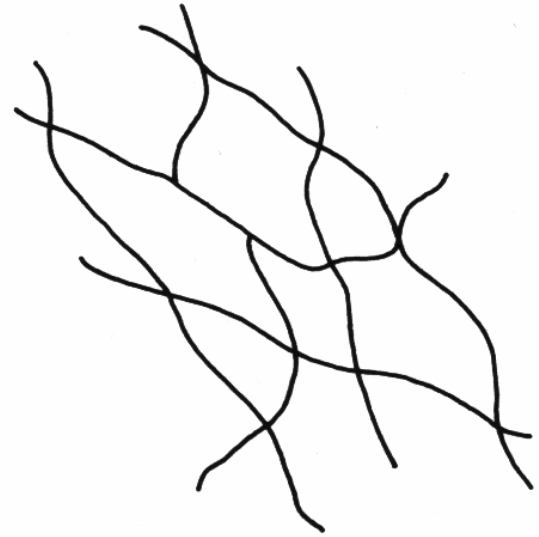
Network polymers have three-dimensional structures in which each chain is connected to all others, and are characterized by their crosslinking density or degree of crosslinking (number of junction points per unit volume).



Linear



Branched



Network

Homopolymers: Polymers whose structure can be represented by multiple repetition of a single type of **repeat unit** which may contain one or more species of **monomer unit**.

$-(M)_n-$ M: monomer unit or repeat unit;
 n : **number of repeat units** or
degree of polymerization (DP)

$n = 2$ (dimer), 3 (trimer), 4 (tetramer), 5
(pentamer), 6 (hexamer),

< 20: oligomer (e.g., MW < 2,000)
> 20 or MW >10,000: polymer

Nomenclature

Source-based nomenclature places the prefix *poly* before the name of the monomer, the monomer's name being contained within parentheses unless it is a simple single word [e.g., poly(methyl methacrylate) (PMMA), polyethylene (PE)].

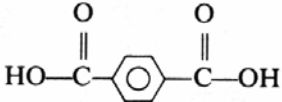
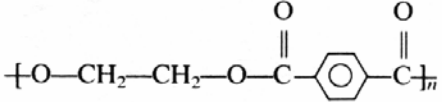
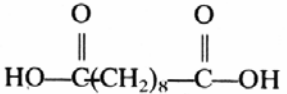
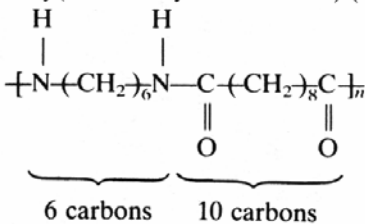
In **structure-based nomenclature** the prefix *poly* is followed in parentheses by words which describe the chemical structure of the repeat unit [e.g., poly(ethylene terephthalate) (PET)].

Polyesters:	$-(O-R-CO)_n-$ or $-(O-R-O-CO-R'-CO)_n-$
e.g.,	HO-R-OH + HOCO-R'-COOH (diol + diacid)
Polycarbonates:	$-(O-R-O-CO)_n-$
e.g.,	HO-R-OH + COCl ₂ (diol + phosgene)
Polyamides:	$-(NH-R-CO)_n-$ or $-(NH-R-NH-CO-R'-CO)_n-$
e.g.,	NH ₂ -R-NH ₂ + HOCO-R'-COOH (diamine + diacid)
Polyurethanes:	$-(O-R-O-CO-NH-R'-NH-CO-)_n-$
e.g.,	HO-R-OH + OCN-R'-NCO (diol + diisocyanate)
Polyureas:	$-(NH-R-NH-CO-NH-R'-NH-CO-)_n-$
e.g.,	NH ₂ -R-NH ₂ + OCN-R'-NCO (diamine + diisocyanate)
Polysiloxanes:	$-[Si(R_2)-O]_n-$ (silicones)

TABLE 1.1 *continued*

Monomers	Polymer	Comments
(5) Methyl methacrylate $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C} \\ \\ \text{C}=\text{O} \\ \\ \text{OCH}_3 \end{array}$	Poly(methyl methacrylate) (PMMA) $\begin{array}{c} \text{CH}_3 \\ \\ \text{[-CH}_2\text{-C-]}_n \\ \\ \text{C}=\text{O} \\ \\ \text{OCH}_3 \end{array}$	Transparent sheets and mouldings; used for aeroplane windows; more expensive than PS, e.g. 'Perspex', 'Diakon', 'Lucite', 'Oroglass', 'Plexiglas'.
(6) Vinyl chloride $\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{Cl} \end{array}$	Poly(vinyl chloride) (PVC) $\begin{array}{c} \text{[-CH}_2\text{-CH-]}_n \\ \\ \text{Cl} \end{array}$	Water pipes and gutters, bottles, gramophone records; plasticized to make PVC leathercloth, raincoats, flexible pipe and hose, toys, sheathing on electrical cables, e.g. 'Darvic', 'Welvic', 'Vinoflex', 'Hostalit'.
(7) Vinyl acetate $\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{O} \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}$	Poly(vinyl acetate) (PVA) $\begin{array}{c} \text{[-CH}_2\text{-CH-]}_n \\ \\ \text{O} \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}$	Surface coatings, adhesives, chewing gum.

TABLE 1.1 *continued*

Monomers	Polymer	Comments
(8) Ethylene glycol $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$	Poly(ethylene glycol) (PEG) $\text{[-CH}_2-\text{CH}_2-\text{O-}]_n$	Water-soluble packaging films, textile sizes, thickeners, e.g. 'Carbowax'.
(9) Ethylene glycol $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ and terephthalic acid  $\text{HO}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{OH}$	Poly(ethylene terephthalate) (PET)* 	Textile fibres, film, bottles, e.g. 'Terylene', 'Dacron', 'Melinex', 'Mylar'.
(10) Hexamethylene diamine $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$ and sebacic acid  $\text{HO}-\text{C}(=\text{O})-(\text{CH}_2)_8-\text{C}(=\text{O})-\text{OH}$	Poly(hexamethylene sebacate) (nylon 6.10)* 	Mouldings, fibres, e.g. 'Ultradid 6.10'.

* The polymer has two monomer units in the repeat unit.

The word **copolymer** is commonly used to describe polymers whose molecules contain *two or more* different types of repeat unit.

Statistical copolymers are copolymers in which the sequential distribution of the repeat units obeys known statistical laws.

Random copolymers are a special type of statistical copolymer in which the distribution of repeat units is truly random.

~~~B-A-B-B-A-B-A-A-B-A-B-B-B-A~~~

(For simplicity, illustration is for copolymers containing only A and B.)

**Alternating copolymers** have only two different types of repeat unit and these are arranged alternately along the polymer chain:

~~~A-B-A-B-A-B-A-B-A-B-A-B~~~

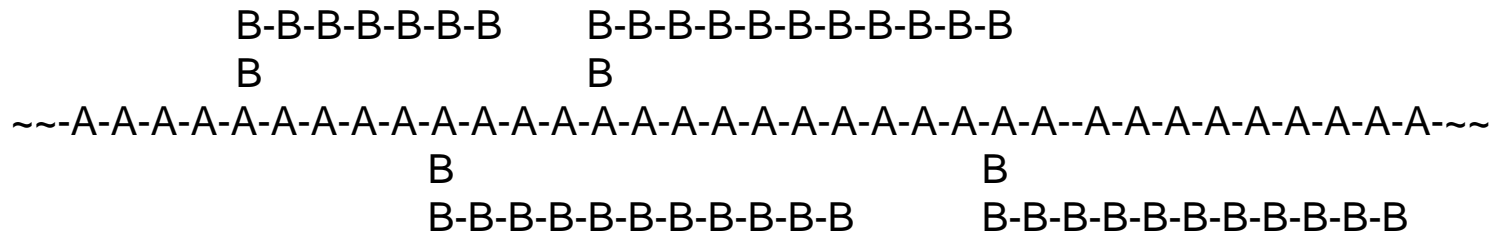
Statistical, random, and alternating copolymers generally have properties which are intermediate to those of the corresponding homopolymers.

Block copolymers are linear copolymers in which the repeat units exist only in long sequences, or blocks, of the same type.

E.g., AB diblock copolymers ~~-A-A-A-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B~~~

ABA triblock copolymers ~~-A-A-A-A-A-A-B-B-B-B-B-B-B-B-A-A-A-A-A~~~

Graft copolymers are branched polymers in which the branches have a different chemical structure to that of the main chain.



Block and graft copolymers usually show properties characteristic of each of the constituent homopolymers. They also have some unique properties arising from the copolymerization.

Nomenclature

Statistical copolymer of ethylene and propylene
poly(ethylene-*stat*-propylene)

ABA triblock copolymer of styrene (A) and isoprene (B)
polystyrene-*block*-polyisoprene-*block*-polystyrene

alternating copolymer of styrene and maleic anhydride
poly[styrene-*alt*-(maleic anhydride)]

Classification of Polymers

Thermosets

Rigid materials and network polymers in which chain motion is greatly restricted by a high degree of crosslinking.

Intractable once formed.

Degrade rather than melt upon heating.

Elastomers

Crosslinked rubbery polymers that can be stretched easily to high extensions and which rapidly recover their original dimensions when the applied stress is released.

Low crosslink density.

Thermoplastics (plastics)

Linear or branched polymers which can be melted upon the application of heat. (Largest proportion of the polymers used in industry.)

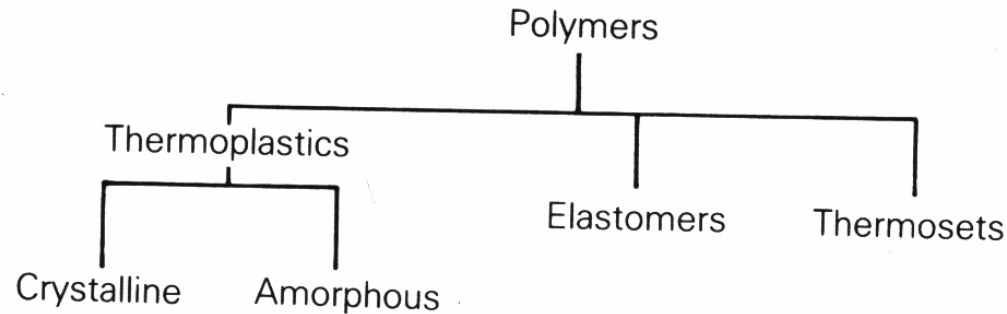


Fig. 1.2 *Classification of polymers.*

Crystalline polymers

Invariably do not form perfect crystalline materials but instead are semicrystalline with both crystalline and amorphous regions. The crystalline phase of such polymers are characterized by their melting temperature (T_m).

Amorphous polymers

Characterized by their glass transition temperature (T_g), the temperature at which they transform abruptly from the glass state (hard) to the rubbery state (soft). This transition corresponds to the onset of chain motion.

Molecular Weight and Polydispersity

Molecular Weight

Molar mass (M): mass of 1 mole of polymer, in unit of g mol^{-1} .
(Practically people use **molecular weight** instead of molar mass.)

$$M = xM_0$$

where x (or n): degree of polymerization, M_0 : molar mass of repeat unit.

Molecular Weight Distribution

With very few exceptions (e.g., some materials of biological origin), polymers consist of macromolecules with a range of molecular weights.

Molecular Weight Averages

To define any arithmetic mean A , let's assume unit volume of a sample of N polymer molecules comprising: N_1 molecules with molecular weight M_1 , N_2 molecules with molecular weight M_2 , ..., N_j molecules with molecular weight M_j .

$$N = N_1 + N_2 + \dots + N_j$$

The arithmetic mean molecular weight A is given as usual by the total measured quality (M) divided by the total number of elements.

$$A = \frac{N_1 M_1 + N_2 M_2 + \dots + N_j M_j}{N_1 + N_2 + \dots + N_j} = \sum (N_i/N) M_i$$

Number-average molecular weight (M_n): "the sum of the products of the molar mass of each fraction multiplied by its mole fraction".

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

The weight fraction w_i is defined as the mass of molecules of molar mass M_i divided by the total mass of all the molecules present

$$w_i = N_i M_i / \sum N_i M_i$$

from which it can be deduced that

$$\sum (w_i / M_i) = \sum N_i / \sum N_i M_i$$

$$M_n = 1 / \sum (w_i / M_i)$$

Number-average degree of polymerization

$$x_n = M_n / M_0$$

Another method of averaging weights the property by mass (usually called weight) of the material having that property.

The **weight-average molecular weight** M_w is defined as "the sum of the products of the molar mass of each fraction multiplied by its weight fraction w_i ".

$$M_w = \sum (w_i M_i) = \sum N_i M_i^2 / \sum N_i M_i$$

Weight-average degree of polymerization

$$x_w = M_w / M_0$$

Z-Average Molecular Weight (z stands for centrifuge. German *zentrifuge*)

$$M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} = \frac{\sum w_i M_i^2}{\sum w_i M_i}$$

Viscosity-Average Molecular Weight

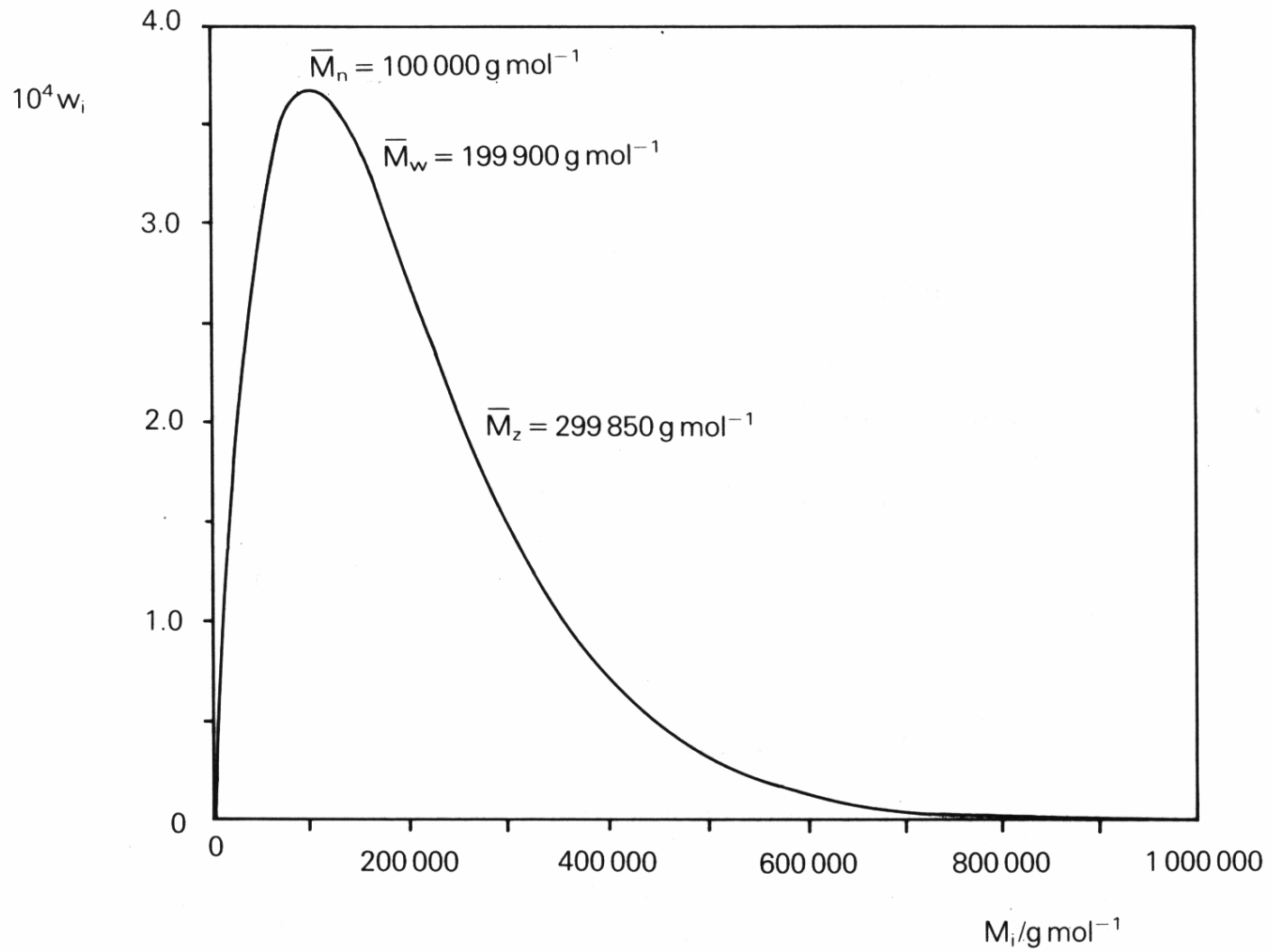
$$M_\eta = \left(\frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right)^{1/a} = \left(\frac{\sum w_i M_i^a}{\sum w_i M_i} \right)^{1/a}$$

Mathematically, $M_n \leq M_w \leq M_z$, here the equality sign holds only for monodisperse polymers.

The ratios of different molecular weight averages M_w/M_n and M_z/M_w are often used as characteristics of polymer **polydispersity**.

For most polymers M_w/M_n : 1.5–2.5

For **monodisperse polymer**: $M_w/M_n = M_z/M_w = 1$



Polymers Are Everywhere

Records

Let's see what polymers we can find at a record store.

The CDs that give you such great sound are made from [polycarbonate](#), a material also used for shatterproof windows.

The case the CD comes in is made of [polystyrene](#).

A cassette tape is made from many parts made from polymers. The housing is made from [polystyrene](#).

The tape itself is a thin film of something or another. Other parts are made from [nylon](#), [polyethylene](#), and other polymers.

The oak CD cabinets are made of wood, and wood is a form of [cellulose](#), a [polysaccharide](#) (natural polymer).

Pharmacy

Diapers are made of [polyethylene](#). They have elastic to keep them from leaking, and that elastic is made from [natural rubber](#).

But most importantly they're packed with [poly\(acrylic acid\)](#). [Poly\(acrylic acid\)](#) is a member of the [acrylate](#) family of polymers. It can absorb many times its own weight in water.

The bristles on a toothbrush were the first things ever made from [nylon](#). Its handle is made of [polyethylene](#).

Clean hair is a good thing, and clean hair comes from shampoos, which have thickeners [hydroxyethyl cellulose](#). Conditioners are made with [silicones](#).

Hair spray is just chock full of polymers like [poly\(vinylpyrrolidone\)](#).

If you hurt your ankle or your knee you might need one of those flexible elastic bandages. They contain natural rubber, [polyisoprene](#).

Auto Parts

A lot of auto body parts are made out of polymer like [ABS](#) plastic.

The tread of a tire is made from a special rubber called [poly\(styrene-butadiene-styrene\)](#). The sidewalls are made of another rubber called [polyisoprene](#). And the inner liner is made of another kind of rubber called [polyisobutylene](#).

Also, the tires are reinforced with cords made from [Kevlar](#), which is also used to make bullet-proof vests.

A windshield wiper and its blade is made from a rubber called [polyisoprene](#).

Headlights can have lenses made from [polycarbonate](#).

A hose is made from a rubber [polybutadiene](#).

An air filter is made mostly of heavy paper ([cellulose](#)) and of polymers like [polyisoprene](#).

A gas can is made from [polyethylene](#). And lastly we have some carpeted floor mats made from [nylon](#).

Electronics

Electrical cables are insulated with polymers like [polyethylene](#) and [polyisoprene](#). For wires that get really hot, we use insulation made from a fireproof polymer called [poly\(vinylidene fluoride\)](#).

The cases of CD players and amplifiers are also made of plastics such as [polystyrene](#). If you take the covers off your CD players or your computers, you'll find that inside, the circuit boards are made of [epoxy resins](#).

Cones of high quality speakers like subwoofer are made of a plastic called [polypropylene](#).

The piezoelectric tweeters contain [poly\(vinylidene fluoride\)](#). An alternating field makes it vibrate, and the vibration can be made to produce sound.

The mesh fabric that covers the speaker is made of [nylon](#), and it's stretched over a [polystyrene](#) frame.

The outside housing of a telephone set is made from a special kind of [polystyrene](#), high-impact [polystyrene](#). It's a graft copolymer of [polystyrene](#) with a rubbery polymer, [polybutadiene](#). It's much less brittle than regular [polystyrene](#).

Eyeball Bonanza

In the old days, eyeglasses were made of glass. But for some people with really bad eyesight, glass lenses would just be way too thick and heavy. Also when you're a destructive child with bad eyesight, glass doesn't stay unbroken for very long.

So nowadays eyeglasses are often made of a special kind of [polycarbonate](#) that's a lot lighter than glass. Also it has a higher refractive index, so really strong lenses don't have to be nearly so thick, which is great for the people who can't see very well.

There're also polymers in contact lenses. A long time ago people wore hard contact lenses, made of [poly\(methyl methacrylate\)](#). But these were uncomfortable, and along came much more comfortable soft contact lenses, made from [poly\(acrylamides\)](#).

Camera

The film is made from things like [polyester](#). But in the old days, it was made from something called [cellulose nitrate](#). The problem with cellulose nitrate is that it is flammable. Hot projector bulbs often made it catch on fire, and in the olden days many theaters burned down in this way.

The filters are made of a hard, transparent polymer called [polycarbonate](#). They're used for making nifty effects, and such in your photographs by filtering out certain colors of light.

Long ago before every camera had a built-in flash there were things called flash cubes. The clear plastic on the outside is [polyethylene](#). The reflectors are made of [polystyrene](#).

In the odd event that any of your pictures are worth looking at, you may want to keep them in a photo album. The simulated leather cover is made of [PVC](#).

And many of the housings of the cameras themselves are made of plastics like [polystyrene](#). Clear polystyrene is also used for flash lenses.

Shoes

A running shoe has panels made of leather, and also of [nylon](#). The sole is made out of a hard rubber called [SBS rubber](#). A lot of the same stuff goes into a hiking boot, including insole padding made from [polyurethane](#) foam.

Shoe laces are made from things like [nylon](#) and [cotton](#).

Pricier dress shoes are made of [leather](#), but inexpensive pumps are often skinned with [poly\(vinyl chloride\)](#).

Duck shoes are good at keeping your feet dry on rainy days because they're made out of natural rubber, [polyisoprene](#).

We wouldn't have socks without polymers like [cotton](#), and synthetics like [polyester](#) and [nylon](#). Also, they stay up with the help of elastic thread, which contains another natural polymer, [natural rubber](#).

Pool

There's so many polymers in a pool: we're practically swimming in them! First of all, there are those goggles we're wearing. They contain a lot of rubber materials like [polyisoprene](#) and [polybutadiene](#). Sometimes even the lenses are made of polymers like [polycarbonate](#).

Swimming is fun, but drowning isn't. A life preserver can keep that from happening. It is made of styrofoam, which is a form of [polystyrene](#). The rope around it is also made of polymers. It's made of [nylon](#). Nylon stands up to water better than cotton or hemp rope.

With those [nylon](#) nets we can keep leaves and dead bugs out of the pool.

Clothes

Blue jeans and T-shirts are made of cotton, a form of [cellulose](#).

Sweaters can be made from [wool](#), which is another form of collagen (so being your skin and hair). Sweaters are also made out of [acrylics](#), like [poly\(acrylonitrile\)](#) or [rayon](#).

Socks are made out of a lot of the same polymers as sweaters. Also, to keep them from falling down, socks sometimes have a little bit of spandex in them. Spandex is a kind of [polyurethane](#).

Bicycle pants and other items of stretchwear are made of spandex.

All of the clothing is made of polymers in the form of [fibers](#).

Paint and Decorating

The carpet is made from [nylon](#). The padding underneath is a foam made of [polyurethane](#).

In the kitchen and bathroom, things can get kind of wet, and carpet could get kind of nasty with all that water around. So for kitchens and bathroom floors there is linoleum, which is made of [poly\(vinyl chloride\)](#) plastic.

There is indoor/outdoor carpeting. Because it's made of [polypropylene](#) it can stand up to rain and humidity and all kinds of outdoor water.

Kitchen counters can also be made of polymers. Most are made of [melamine-formaldehyde resin](#).

A gray countertop is made of a special material. In kitchens where heat resistance is important (think of setting hot pots down on your counter) are made of [poly\(methyl methacrylate\)](#) blended with aluminum oxides.

Acrylic paint isn't made of polymers. But it does contain a something called methyl methacrylate. After you slap this stuff on your walls that methyl methacrylate will react to form [poly\(methyl methacrylate\)](#). Acrylic latex paints also have copolymers of [poly\(vinyl acetate\)](#).

Sportin' Stuff

A basketball has an outer cover made from [leather](#), a natural polymer. To help it hold air it has an inner liner made from a kind of rubber [polyisobutylene](#).

Baseball gloves are also made of leather, and that leather is stitched together with thread made from polymeric fibers, such as [nylon](#) and [polyesters](#).

The frame of a tennis racket is made from an especially strong polymer called carbon fiber, and its strings are made of [nylon](#).

Biking shorts are made of fibers of an interesting block copolymer called spandex, which allows the pants to stretch.

The cover of a golf ball is often made of Surlyn. This is a kind of material we call an ionomer or a thermoplastic elastomer.

Toys

A toy flying squirrel is made out of [polyisoprene](#) rubber and [polyurethane](#) foam.

All the critters like zebra, rhinoceros, tree frog, brachiosaurus, ... are made of [polyisoprene](#).

Keeping with the animal theme, many puppets are stuffed with [polyurethane](#) foam. On the outside their fur, be they mammals, is made of things like [polyacrylonitrile](#). Their scales, be they fish, are made of [nylon](#).

Like to play with robots? A robot may be made of [polystyrene](#). The wires have insulation made out of things like [polyethylene](#) and [polyisoprene](#). Inside there are circuit boards, which are often made from [epoxy resins](#).

More grown children play with rc cars than do the little ones. A rc car normally has a body made of [polystyrene](#) and tires made of [polyisoprene](#).

Finally we have a thresher shark, which is made of [polyethylene](#).

Hardware

Cellulose is the major component of wood. This polymer is so common it grows on trees.

As for plywood, its sheets are glued together with adhesives made from polymers like **poly(vinylpyrrolidone)**. Plywood is what we call a composite material, that is a material made of more than one component.

There is nothing that duct tape can't do. So what is it? It is a composite of a sheet of **polyethylene** tape reinforced by a mesh of cotton.

If your house has indoor plumbing, it probably has **poly(vinyl chloride)** pipe somewhere underneath the sinks.

Many storm windows are made from polymers **poly(methyl methacrylate)** and **polycarbonate**. The frame is often made of **poly(vinyl chloride)**.

Both storm windows and bathtubs are made watertight with **silicone** caulking.