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Advanced Polymer Physics
高等高分子物理

Chapter 1

An Introduction to Polymer Science

Lecture notes by Prof. E. M. Woo - adapting from:

Textbook:

Physical Polymer Science

(Ed: L. H. Sperling, 3rd Ed)

Online Lecture Notes posted on:

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Chap 1. **INTRODUCTION TO POLYMER SCIENCE**

- Polymer science was born in the great industrial laboratories of the world of the need to make and understand new kinds of **plastics, rubbers, adhesives, fibers, resins, and paints**.

- Only much later did polymer science come to **academic life**. Perhaps because of its origins, polymer science tends to be more **interdisciplinary** than most sciences, combining **chemistry, chemical engineering, materials, and other fields** as well.

- Chemically, polymers are long-chain molecules of very high molecular weight, often measured in the hundreds of thousands. For this reason, the term "**macromolecules**" is frequently used when referring to polymeric materials.

Preface

- This book develops the **subject of physical polymer science**, describing the inter-relationships among polymer **structure**, **morphology**, and **physical, and mechanical behavior**. [i.e., from micro structures to macro-properties]

- Key aspects include molecular weights and molecular weight distribution, and the organization of the atoms down the polymer chains – Configurations, Structures, Crystals, Phases, liquid crystals, structure-property relationships, characterization of structures and morphology, applications of polymers, blends or their nanocomposites, etc.

preface

- Many polymers **crystallize**, and the size, shape, and organization of the crystallites depend on how the polymer was crystallized. Such effects as annealing are very important, as they have a profound influence on the final state of molecular organization.

- Other polymers are **amorphous**, often because their chains are too irregular to permit regular packing. The onset of chain molecular motion heralds the glass transition and softening of the polymer from the glassy (plastic) state to the rubbery state.

- **Mechanical behavior** includes such basic aspects as **modulus, stress relaxation, and elongation to break**. Each of these is relatable to the polymer's basic molecular structure and history.

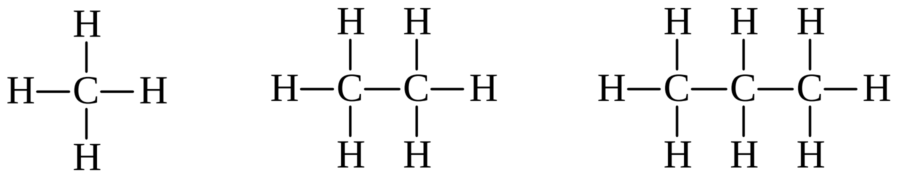
INTRODUCTION: This chapter provides the student with a brief introduction to the broader field of polymer science.

- Although physical polymer science does not include **polymer synthesis**, some knowledge of how polymers are made is helpful in understanding **configurational aspects**, such as **tacticity**, which are concerned with how the atoms are organized along the chain. Similarly, polymer **molecular weights and distributions** are controlled by the synthetic detail.

- **This chapter starts at the beginning of polymer science,** and it assumes no prior knowledge of the field.

1.1 FROM LITTLE MOLECULES TO BIG MOLECULES

- The behavior of polymers represents a continuation of the behavior of smaller molecules at the limit of very high molecular weight. As a simple example, consider the normal alkane hydrocarbon series



$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array} \qquad \begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C & -H \\ & | & | & \\ & H & H & \end{array} \qquad \begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ H- & C- & C- & C & -H \\ & | & | & | & \\ & H & H & H & \end{array} \tag{1.1}$$

Methane Ethane Propane

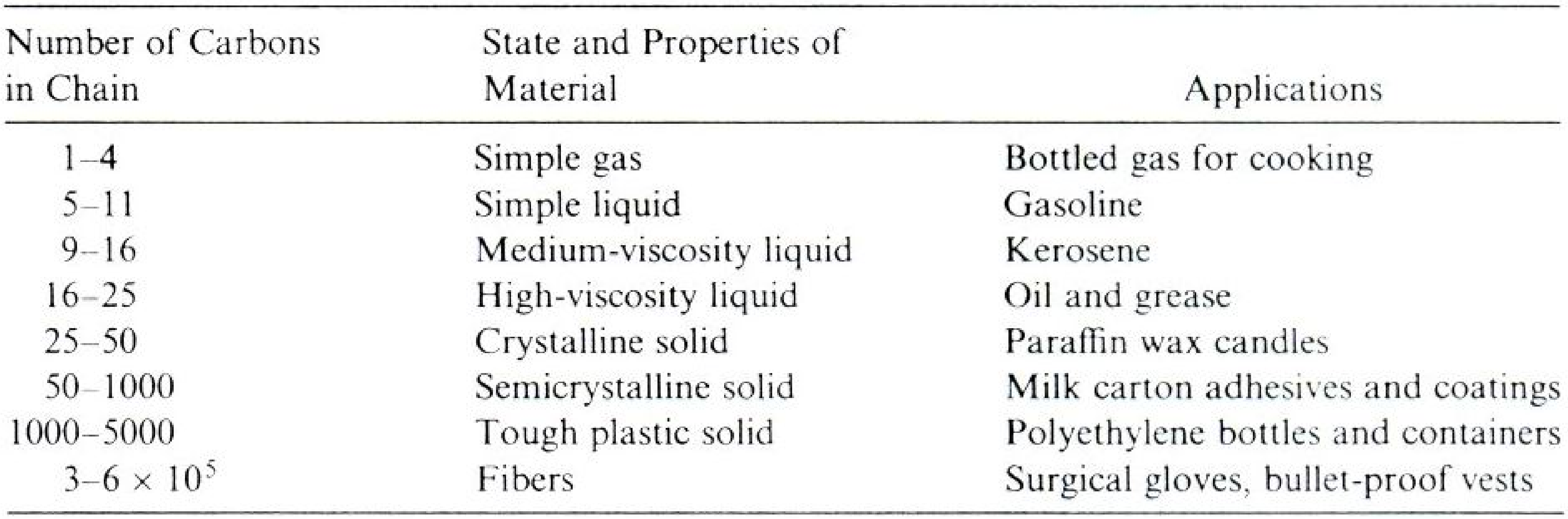
- These compounds have the general structure

$$H\left(CH_2\right)_n H \tag{1.2}$$

where the number of - CH_2 - groups, n, is allowed to increase up to several thousand.

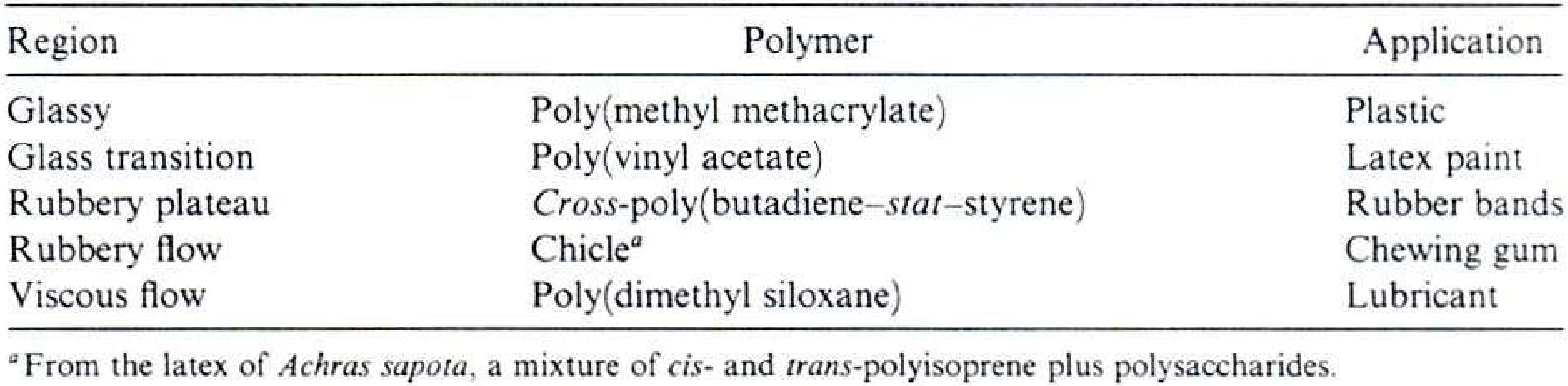
- The progression of their state and properties is shown in **Table 1.1**.

Table 1.1 Properties of the alkane/polyethylene series



Number of Carbons in Chain	State and Properties of Material	Applications
1–4	Simple gas	Bottled gas for cooking
5–11	Simple liquid	Gasoline
9–16	Medium-viscosity liquid	Kerosene
16–25	High-viscosity liquid	Oil and grease
25–50	Crystalline solid	Paraffin wax candles
50–1000	Semicrystalline solid	Milk carton adhesives and coatings
1000–5000	Tough plastic solid	Polyethylene bottles and containers
$3–6 \times 10^5$	Fibers	Surgical gloves, bullet-proof vests

Table 1.2 Typical polymer viscoelastic behavior at room temperature



Region	Polymer	Application
Glassy	Poly(methyl methacrylate)	Plastic
Glass transition	Poly(vinyl acetate)	Latex paint
Rubbery plateau	*Cross*-poly(butadiene–*stat*–styrene)	Rubber bands
Rubbery flow	Chicle[a]	Chewing gum
Viscous flow	Poly(dimethyl siloxane)	Lubricant

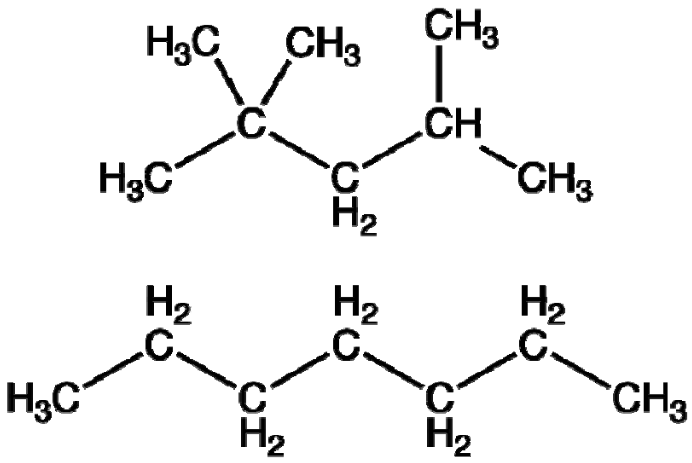
[a] From the latex of *Achras sapota*, a mixture of *cis*- and *trans*-polyisoprene plus polysaccharides.

Note: “Octane number” in gasoline (A mixture):

The octane rating of gasoline is measured in a test engine and is defined by comparison with the mixture of 2,2,4-trimethylpentane (iso-octane) and heptane that would have the same anti-knocking capacity as the fuel under test: the percentage, by volume, of 2,2,4-trimethylpentane in that mixture is the octane number of the fuel.

For example, petrol with the same knocking characteristics as a mixture of 90% iso-octane and 10% heptane would have an “octane rating” of 90.[2]

A rating of 90 does not mean that the petrol contains just iso-octane and heptane in these proportions but that it has the same detonation resistance properties (generally, petrol sold for common use never consists solely of iso-octane and heptane; it is a mixture of several different hydrocarbons, and often other additives).



Isooctane (upper) has an “octane rating” of 100, whereas n-heptane has an octane rating of 0.

Discussion on **Table 1.1**

- At room temperature, the first four members of the series are gases. ***n*-Pentane** boils at 36.1^{o}C and is a low-viscosity liquid. As the molecular weight of the series increases, the viscosity of the members increases. Although commercial gasolines contain many branched-chain materials and aromatics as well as straight-chain alkanes, the viscosity of gasoline is markedly lower than that of **kerosene, motor oil**, and **grease** because of its lower average chain length.

- These latter materials are usually **mixtures of several molecular species**, although they are easily separable and identifiable. → **This point is important because most polymers are also "mixtures";** that is, they have a molecular weight distribution.
- In high polymers, however, it becomes difficult to separate each of the molecular species, and people talk about **molecular weight averages for polymers**.

Cont’d – discussion on Table 1.1

- Compositions of normal alkanes averaging more than about 20 to 25 carbon atoms are **crystalline** at room temperature. These are simple solids known as **wax**. It must be emphasized that at up to **50 carbon** atoms (Mw=?) the material is far from being polymeric in the ordinary sense of the term.

- The polymeric alkanes with no side groups that contain **1000 to 3000 carbon atoms** are known as polyethylenes (PE).

Polyethylene has the chemical structure:

$$H\left(CH_2-CH_2\right)_n H \qquad (1.3)$$

Cont’d

which originates from the structure of the monomer ethylene, $CH_2 = CH_2$. The quantity n is the number of **mers** - or **monomeric units** in the chain. In some places, the structure is written

$$-\!\left(\mathrm{CH_2}\right)\!\!-_{n} \tag{1.4}$$

or **polymethylene**. (Then $n' = 2n$.) The relationship of the latter structure to the alkane series is clearer. While true alkanes have **CH_3 - as end groups**, **most polyethylenes have initiator residues.**

- Even at a chain length of thousands of carbons, the melting point of polyethylene is still slightly molecular-weight-dependent, but most linear polyethylenes have melting or fusion temperatures, T_f, **near 140°C**.
- The approach to the theoretical asymptote of about 145°C at infinite molecular weight (I) is illustrated schematically in **Figure 1.1** (next page).

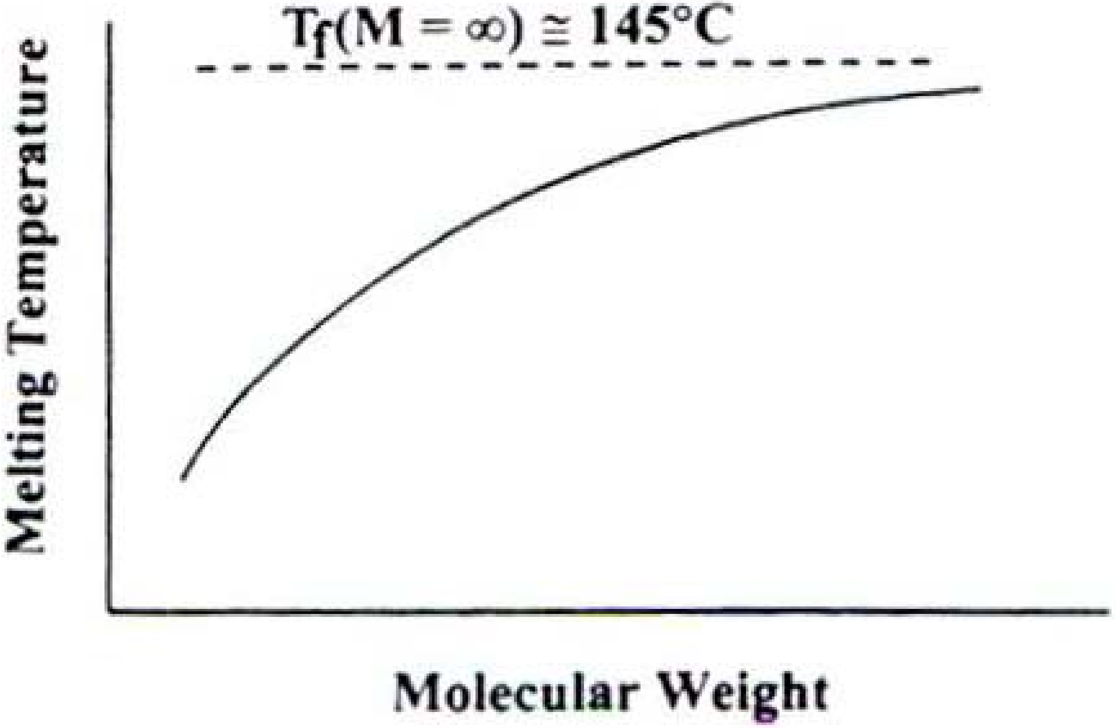
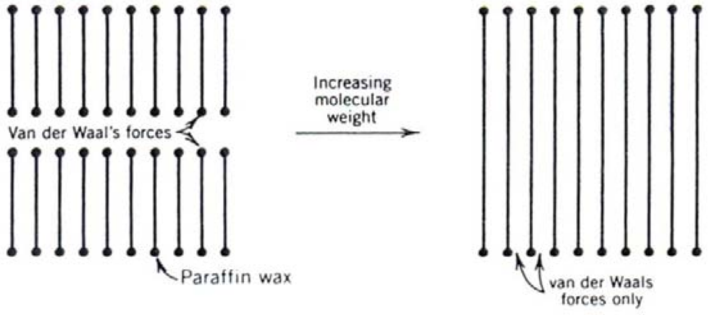


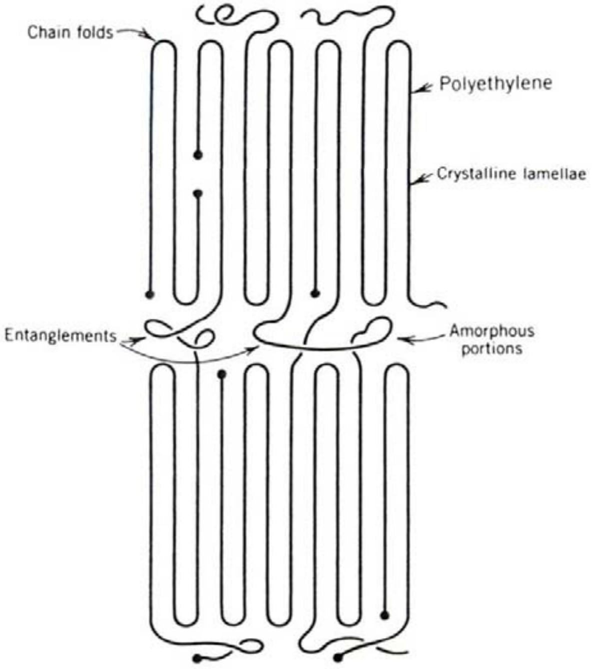
Figure 1.1 The molecular weight-melting temperature relationship for the alkane series. An asymptotic value of about 145^{o}C is reached for very high molecular weight linear polyethylenes.

Wax vs. PE $-(CH_2)_n-$

- The greatest differences between **polyethylene** and **wax** lie in their **mechanical behavior**, however. **While wax is a brittle solid, polyethylene is a tough plastic.** Comparing resistance to break of a child's birthday candle with a wash bottle tip, both of about the same diameter, shows that the wash bottle tip can be repeatedly bent whereas the candle breaks on the first deformation.



- **Polyethylene** is a **tough** plastic solid because its **chains** are long enough to connect individual stems together within a lamellar crystallite by chain folding (see **Figure 1.2 -next**). **The chains also wander between lamellae, connecting several of them together**. These effects add strong covalent bond connections both within the lamellae and between them.
- →On the other hand, only weak van der Waals forces hold the chains together in **wax**.



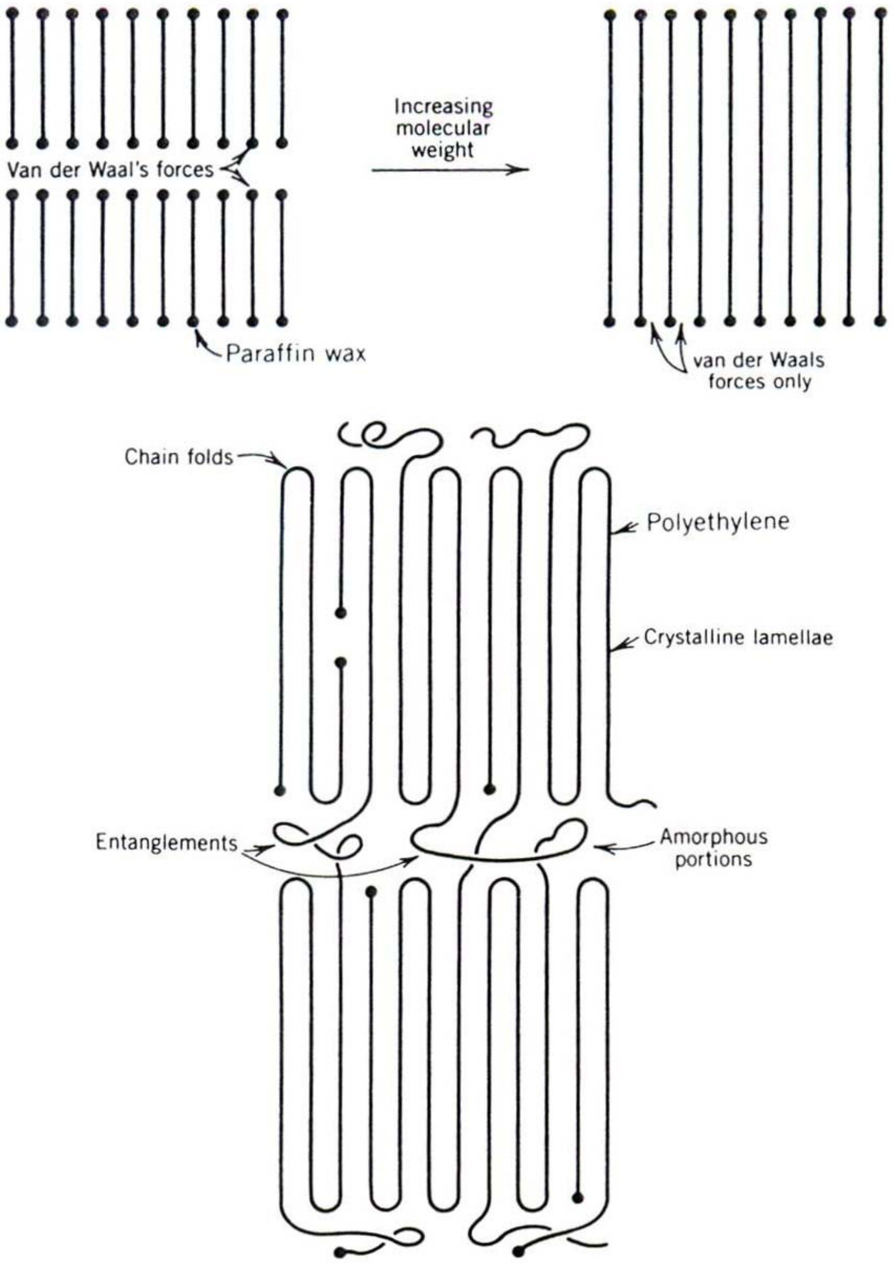


Figure 1.2
Comparison of wax and polyethylene structure and morphology.

- In addition, **a certain portion of polyethylene is amorphous**. The chains in this portion are rubbery, imparting flexibility to the entire material.
- **Wax is 100% crystalline, by difference**.

- The long chain length allows for **entanglement** (see Figure 1.3). **The entanglements help hold the whole material together under stress. In the melt state, chain entanglements cause the viscosity to be raised very significantly also.**

- The long chains shown in **Figure 1.3** also illustrate the **coiling** of polymer chains in the amorphous state. **One of the most powerful theories in polymer science (2) states that the conformations of amorphous chains in space are random coils; that is, the directions of the chain portions are statistically determined.**

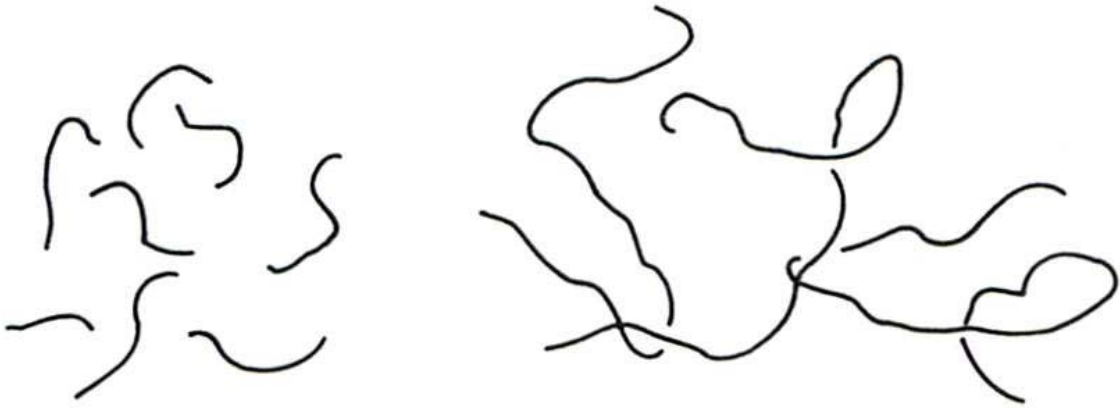


Figure 1.3 Entanglement of polymer chains. (a) Low molecular weight, no entanglement (b) High molecular weight, chains are entangled. The transition between the two is often at about 600 backbone chain atoms.

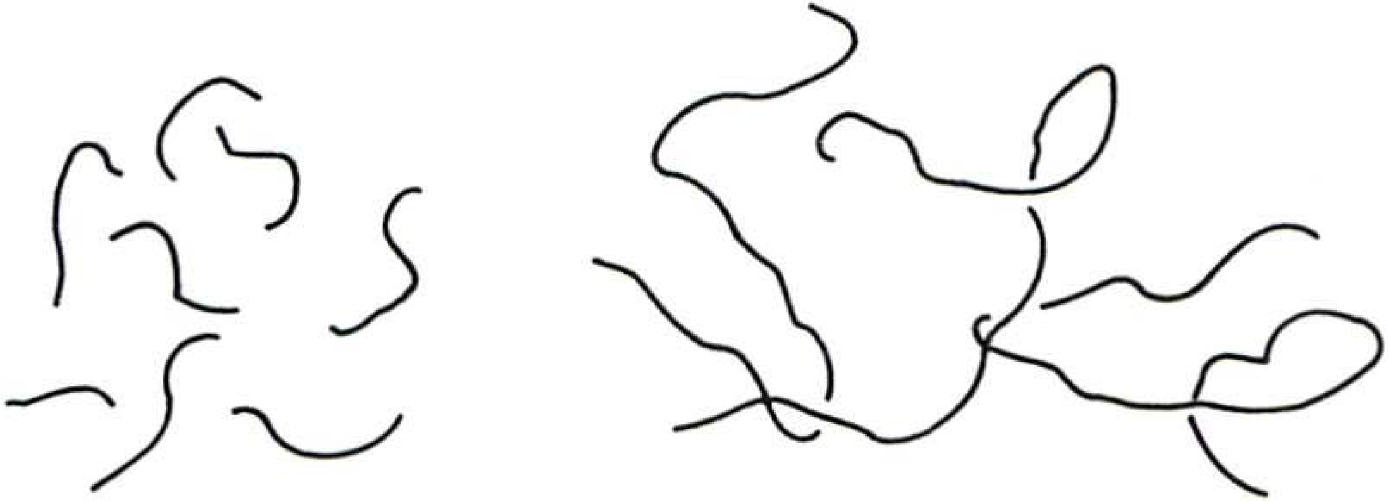


Figure 1.3 Entanglement of polymer chains.
(a) Low molecular weight, no entanglement
(b) High molecular weight, chains are entangled. The transition between the two is often at about 600 backbone chain atoms.

1.2 MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTIONS

While the exact molecular weight required for a substance to be called a polymer is a subject of continued debate, often polymer scientists put the number at about **25,000 g/mol**.

→This is the minimum molecular weight required for **good physical and mechanical properties** for many important polymers.

→This molecular weight (**25,000 g/mol)** is also near the **onset of entanglement**.

1.2.1 Effect on Tensile Strength

- The **tensile strength** of any material is defined as the stress at break during elongation, where stress has the units of **Pa**, dyn/cm^2, or lb/in^2; see Chapter 11. The effect of molecular weight on the tensile strength of polymers is illustrated in **Figure 1.4.**
- At very low molecular weights, the tensile stress to break, σ_b, is near zero. As the molecular weight increases, the tensile strength increases rapidly, and then gradually levels off. Since a major point of weakness at the molecular level involves the chain ends, which do not transmit the covalent bond strength, it is predicted that the tensile strength reaches an asymptotic value at infinite molecular weight.

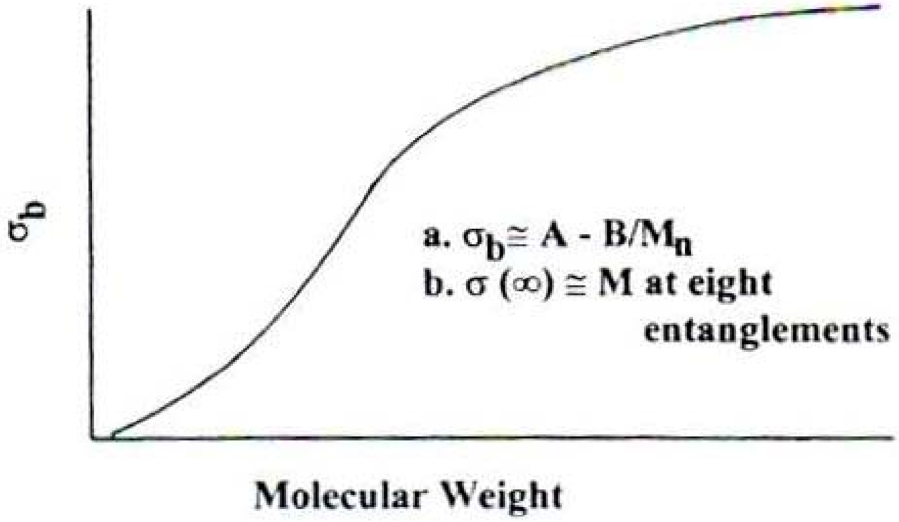


Figure 1.4
Effect of polymer molecular weight on tensile strength.

A large part of the curve in **Figure 1.4** can be expressed (3,4)

$$\sigma_b = A - \frac{B}{M_n}$$

where M_n is the number-average molecular weight (see below) and A and B are constants.

Newer theories by Wool (3) and others suggest that more than 90% of tensile strength and other mechanical properties are attained *when the chain reaches eight entanglements in length.*

1.2.2 Molecular Weight Averages

- The same polymer from different sources may have different molecular weights. Thus polyethylene from source-A may have a molecular weight of 150,000 g/mol, whereas polyethylene from source-B may have a molecular weight of 400,000 g/mol (see **Figure 1.5**). To compound the difficulty, all common synthetic polymers and most natural polymers (except proteins) have a distribution in molecular weights. That is, some molecules in a given sample of polyethylene are larger than others.
- The differences result directly from the kinetics of polymerization.

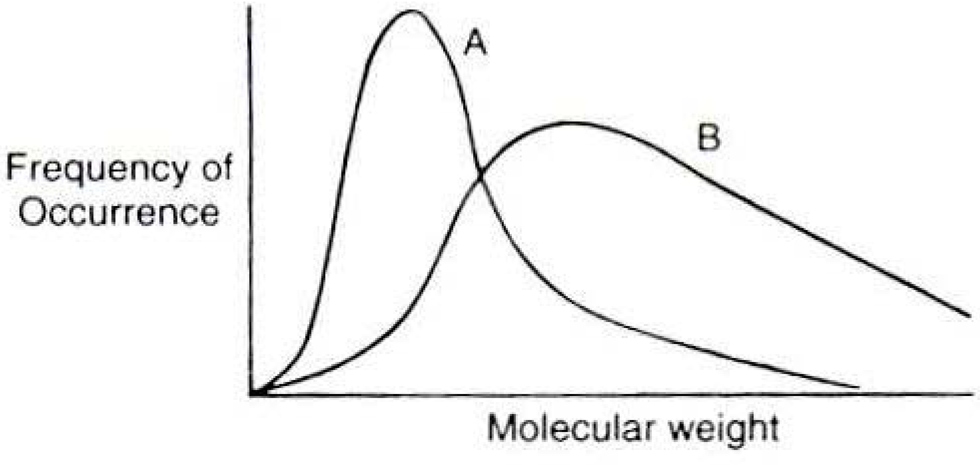


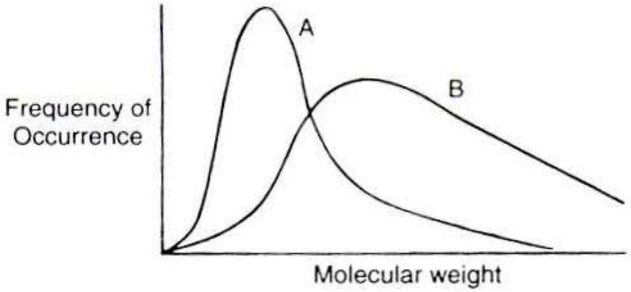
Figure 1.5
Molecular weight distributions of the same polymer from two different sources, A and B.

Mw for polymers – cont’d

- **However, these facts led to much confusion for chemists early in the twentieth century**. At that time chemists were able to understand and characterize **small molecules.**

- Compounds such as hexane all have **six carbon** atoms.

- If polyethylene with **2430 carbon** atoms were declared to be "polyethylene," how could that component having **5280 carbon atoms** also be polyethylene?
- → How could two sources of the material having different average molecular weights both be polyethylene, noting A and B in Figure 1.5?



Molecular weight averages

- The answer to these questions lies in defining average molecular weights and molecular weight distributions (5,6). The two most important molecular weight averages are the **number-average** molecular weight, M_n,

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \quad (1.6)$$

- Where N_i is the number of molecular weight M_i, and the **weight-average** molecular weight, M_w,

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \quad (1.7)$$

For single-peaked distributions, M_n is usually near the peak. The weight-average molecular weight is always **larger**. For simple distributions, M_w may be 1.5 to 2.0 times M_n.

The ratio M_w / M_n, sometimes called the **polydispersity index (PDI)**, provides a simple definition of the molecular weight distribution.

→ Thus, all compositions of $–(CH_2 -CH_2)-_n$ are called “polyethylene”, the molecular weights being specified for each specimen.

Mw distribution and properties/processing, etc.

- For many polymers, a **narrower molecular distribution yields better properties.**

- Reason: The low end of the distribution may act as a plasticizer, softening the material. Certainly it does not contribute as much to the tensile strength.
- The high-molecular-weight tail increases processing difficulties, because of its enormous contribution to the melt viscosity.

- → For these reasons, great emphasis is placed on characterizing polymer molecular weights.

1.3 MAJOR POLYMER TRANSITIONS

- Polymer crystallinity and melting were discussed previously. Crystallization is an example of a first-order transition, in this case **liquid to solid**. Most small molecules crystallize, an example being water to ice. Thus this transition is very familiar.

- A less classical transition is the **glass-rubber transition** in polymers. At the glass transition temperature, T_g, the amorphous portions of a polymer soften. The most familiar example is ordinary **window glass**, which softens and flows at elevated temperatures. Yet, glass is not crystalline, but rather it is an amorphous solid. It should be pointed out that many polymers are totally amorphous.

- Carried out under ideal conditions, the glass transition is a type of "**second-order transition**" (**secondary transition**).

- The basis for the glass transition is the onset of coordinated molecular motion in the polymer chain.

- At low temperatures, only vibrational motions are possible, and the polymer is hard and glassy (**Figure 1.6**, region 1) (7). In the glass transition region, region 2, the polymer softens, the modulus drops three orders of magnitude, and the material becomes rubbery.
- **Regions 3, 4, and 5** are called the rubbery plateau, the rubbery flow, and the viscous flow regions, respectively.
- Examples of each region are shown in **Table 1.2**.

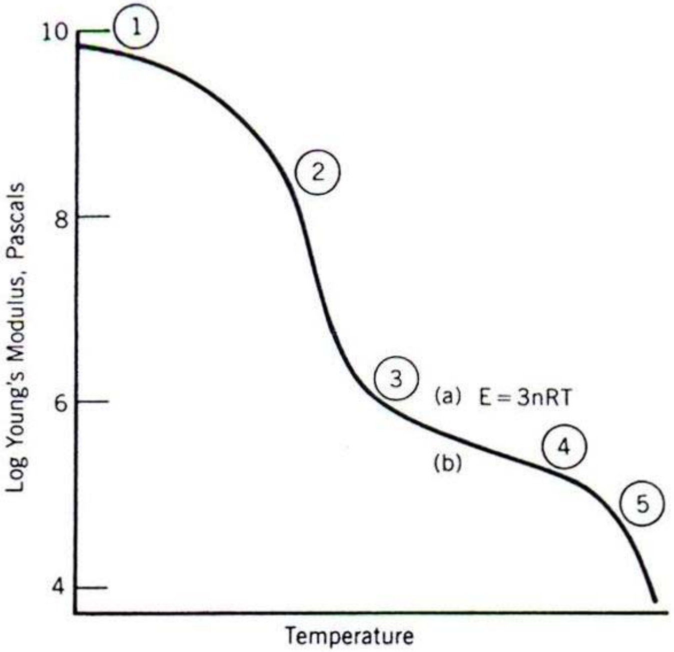


Figure 1.6
Idealized modulus-temperature behavior of an amorphous polymer. Young's modulus, stress/strain, is a measure of stiffness

- **Depending on the region of viscoelastic behavior, the mechanical properties of polymers differ greatly**. Model stress-strain behavior is illustrated in **Figure 1.7** for regions 1, 2, and 3.
- Glassy polymers are stiff and often brittle, breaking after only a few percent extension. Polymers in the glass transition region are more extensible, sometimes exhibiting a yield point (the hump in the tough plastic stress-strain curve). If the polymer is above its brittle-ductile transition, Section 11.2.3, rubber-toughened, **Chapter 13**, or semicrystalline with its amorphous portions above T_g, tough plastic behavior will also be observed. Polymers in the rubbery plateau region are highly elastic, often stretching to 500% or more.
- Regions 1, 2, and 3 will be discussed further in **Chapters 8 and 9**. Regions 4 and 5 flow to increasing extents under stress; see **Chapter 10**.

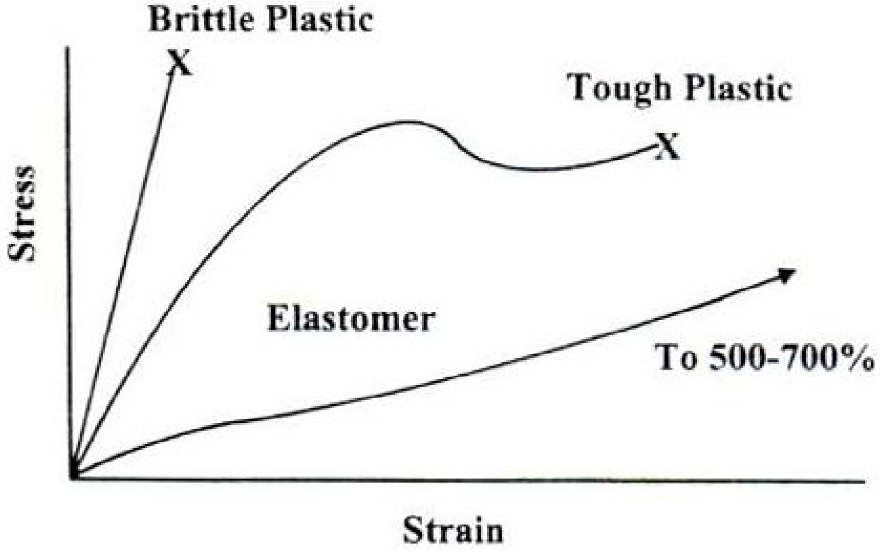


Figure 1.7
Stress-strain behavior of various polymers.

Region 3-Rubbery plateau region

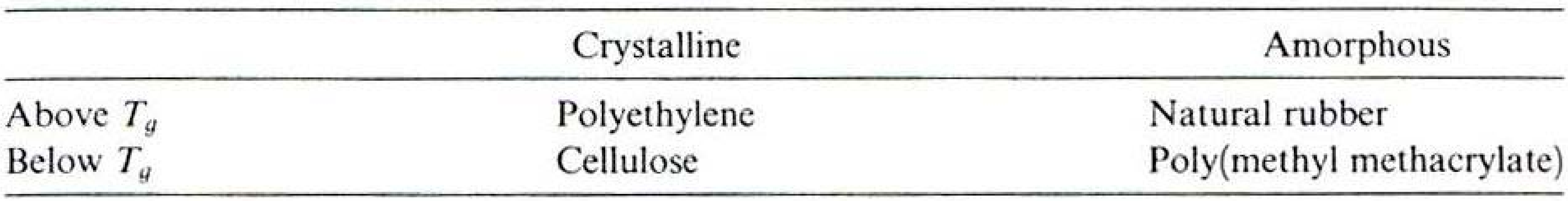
- Crosslinked amorphous polymers above their glass transition temperature behave **rubbery**. Examples are rubber bands and automotive tire rubber.
- In general, Young's modulus of elastomers in the **rubbery-plateau** region is higher than the corresponding linear polymers, and is governed by the relation $E = 3nRT$, in **Figure 1.6.**
- **T**he linear polymer behavior is illustrated by the line (b). Here, ***n*** **represents the number of chain segments bound at both ends in a network**, per unit volume. The quantities R and T are the gas constant and the absolute temperature, respectively.

- Polymers may also be partly crystalline. The remaining portion of the polymer, the amorphous material, may be above or below its glass transition temperature, creating four subclasses of materials.

Applications and transition temperatures

- **Table 1.3** gives a common example of each. While polyethylene and natural rubber need no further introduction, **common names for processed cellulose are rayon and cellophane. Cotton is nearly pure cellulose, and wood pulp for paper is 80-90% cellulose.**
- A well-known trade name for poly(methyl methacrylate) is Plexiglas®. [plastic flexible glass] 壓克力
- The modulus-temperature behavior of polymers in either the rubbery plateau region or in the semicrystalline region are illustrated further in Figure 8.2, **Chapter 8**.

Table 1.3 Examples of polymers at room temperature by transition behavior



	Crystalline	Amorphous
Above T_g	Polyethylene	Natural rubber
Below T_g	Cellulose	Poly(methyl methacrylate)

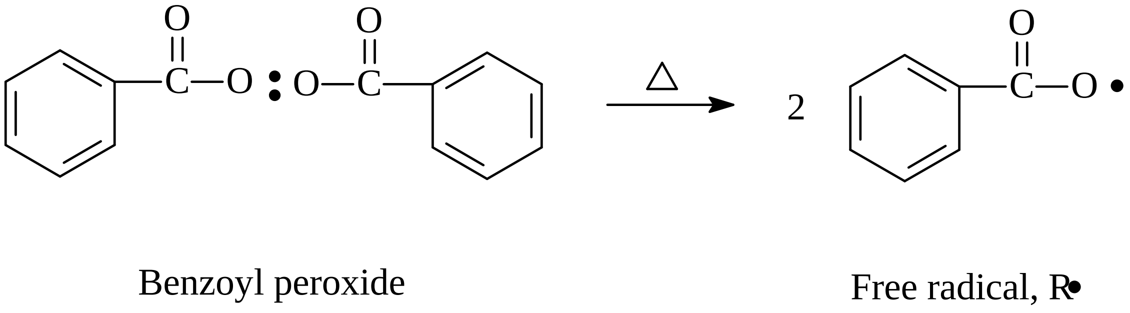
1.4 POLYMER SYNTHESIS AND STRUCTURE

- **1.4.1 Chain Polymerization**
- Polymers may be synthesized by two major kinetic schemes, **chain and stepwise** polymerization.
- The most important of the chain polymerization methods is called **free-radical polymerization**.

- **1.4.1.1 Free Radical Polymerization [chain]**
- The synthesis of poly(ethyl acrylate) will be used as an example of free radical polymerization.
- Benzoyl peroxide is a common initiator. Free radical polymerization has three major kinetic steps - **initiation, propagation, and termination**.

1.4.1.2 Initiation

- On heating, benzoyl **peroxide** decomposes to give two free radicals:

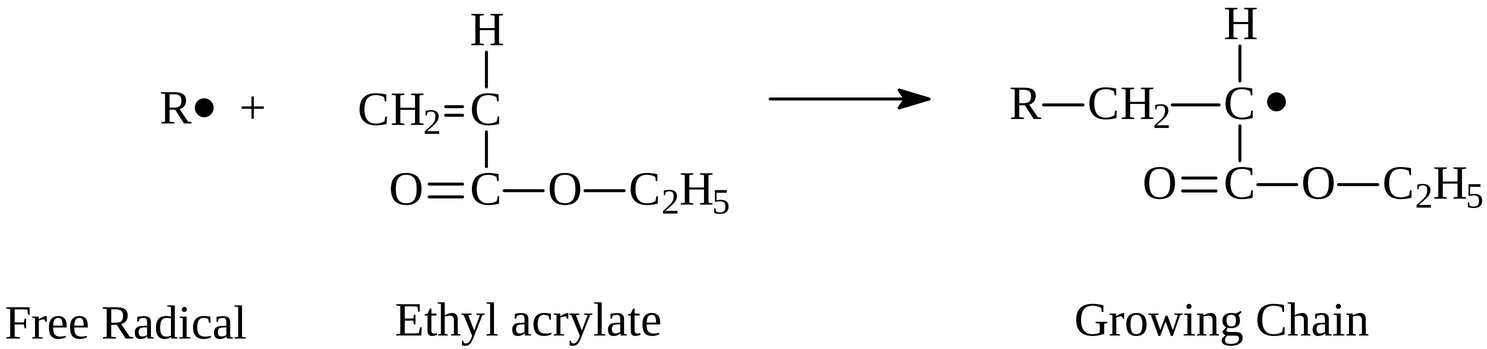


(1.8)

- In this reaction, the electrons in the oxygen bond are unpaired and become the active site. With R representing a generalized organic chemical group, the free radical can be written R·.

(It should be pointed out that **hydrogen peroxide** undergoes the same reaction on a wound, giving a burning sensation as the free radicals "kill the germs.")

- The initiation step usually includes the addition of the first monomer molecule:

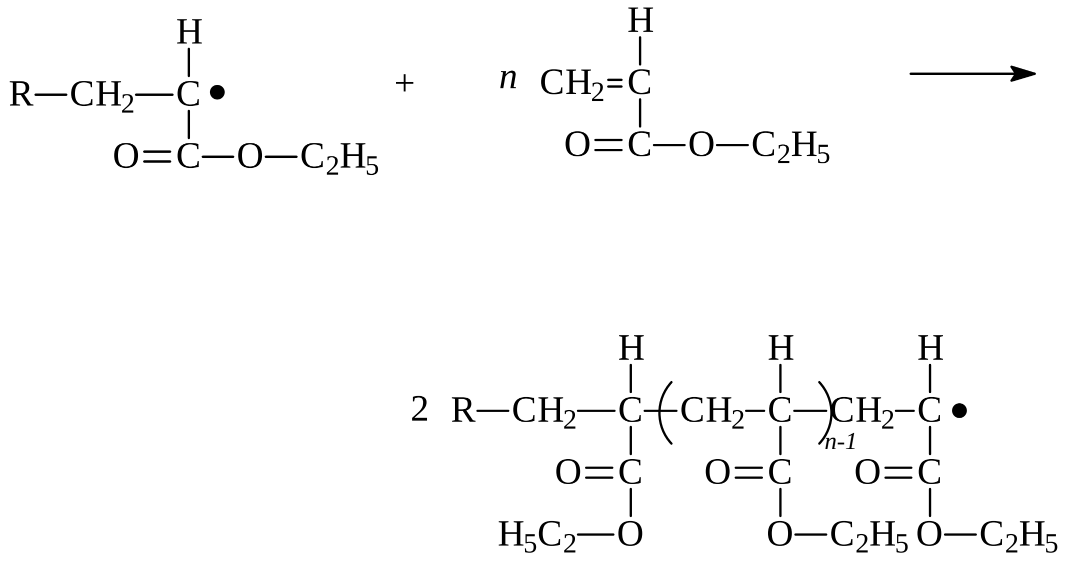


$$R\bullet \;+\; CH_2{=}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O{=}C{-}O{-}C_2H_5}{|}}{C}} \longrightarrow R{-}CH_2{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O{=}C{-}O{-}C_2H_5}{|}}{C}}\bullet \qquad (1.9)$$

- In this reaction, the free radical attacks the monomer and adds to it. The double bond is broken open, and the free radical reappears at the far end.

1.4.1.3 Propagation

After initiation reactions (1.8) and (1.9), many monomer molecules are added rapidly, perhaps in a fraction of a second:



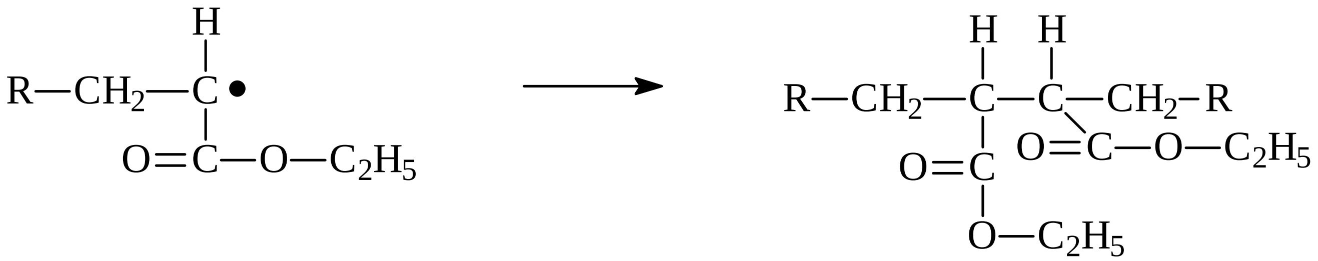
$$R{-}CH_2{-}\overset{H}{\underset{O=C-O-C_2H_5}{C}}\bullet + n\ CH_2{=}\overset{H}{\underset{O=C-O-C_2H_5}{C}} \longrightarrow 2\ R{-}CH_2{-}\overset{H}{\underset{\underset{H_5C_2-O}{O=C}}{C}}{\left(CH_2{-}\overset{H}{\underset{\underset{O-C_2H_5}{O=C}}{C}}\right)}_{n-1}CH_2{-}\overset{H}{\underset{\underset{O-C_2H_5}{O=C}}{C}}\bullet \quad (1.10)$$

On the addition of each monomer, the free radical moves to the end of the chain.

1.4.1.4 Termination

- In the **termination reaction**, two free radicals react with each other.

Termination is either by **combination**,



$$\mathrm{R{-}CH_2{-}\dot{C}H(COOC_2H_5)} \longrightarrow \mathrm{R{-}CH_2{-}CH(COOC_2H_5){-}CH(COOC_2H_5){-}CH_2{-}R} \qquad (1.11)$$

where R now represents a long-chain portion,

or by disproportionation [“out of proportion”], where a hydrogen is transferred from one chain to the other.

Nature’s building blocks for polymers

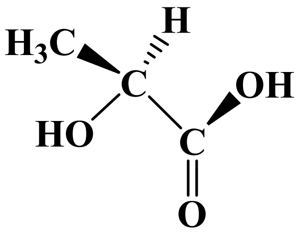
-The best polymers – but cannot be re-produced by syntheses.

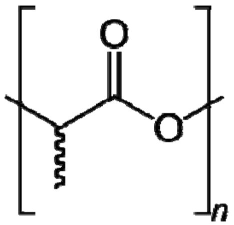
Low-Mw chemicals produced by nature: millions of different structures…….

However, building blocks for polymers in nature – only several major kinds:

$H_2N\text{-}CHR\text{-}COOH$

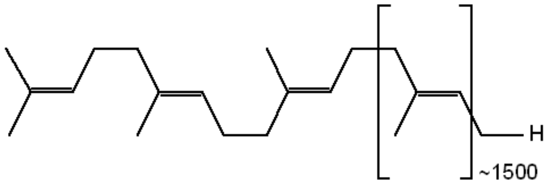
α-Amino acids (**23 different types of R**) – L- and D-forms. →Nature uses these monomers to make DNA, silks, spider webs, body tissues, hairs, nails, tendons, eggs, etc……

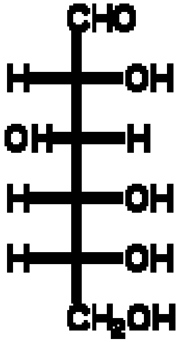




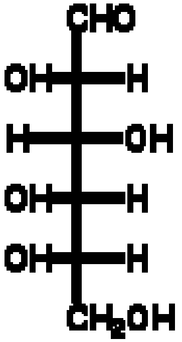
← Lactic acids – L- and D-forms

Terpenes: trans- and cis- form→



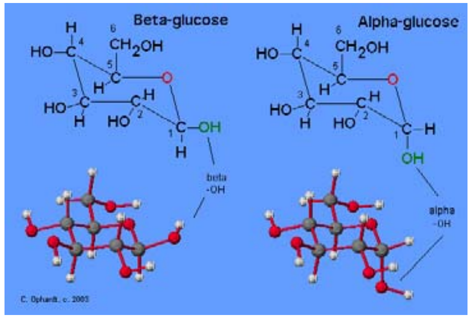


D-glucose



L-glucose

Glucose (D- and L-forms): These monomers are used to make starch, cellulose (cotton, tree trunks, nut-shells, etc.), Glucosamines (glucose+amino acids), keratins, chitins, etc.



Effects of molecular weights on polymer properties:

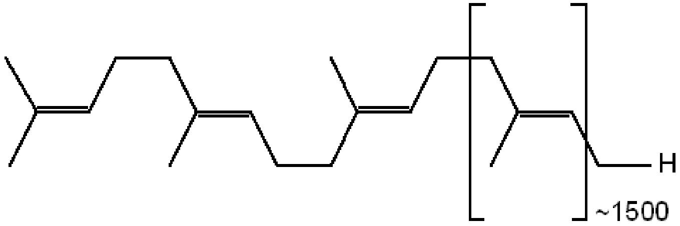
Many properties of cellulose depend on its chain length or degree of polymerization, the number of glucose units that make up one polymer molecule.

Cellulose from wood pulp has typical chain lengths (lower Mw) between 300 and 1700 units;

Cotton and other plant fibers as well as bacterial cellulose have chain lengths (higher Mw) ranging from 800 to 10,000 units.[10]

Molecules with very small chain length resulting from the breakdown of cellulose are known as cellodextrins; in contrast to long-chain cellulose, cellodextrins are typically soluble in water and organic solvents.

Cellodextrins – breakdown of cellulose by bacteria.
Examples of cellodextrins are:
cellobiose (DP=2) (sometimes not included in cellodextrin classification)
cellotriose (DP=3)
cellotetraose (DP=4)
cellopentaose (DP=5)
cellohexaose (DP=6)



Amber: - a nature's macromolecule.
From fossilized tree resins (terpene+others) under high pressure and millions of years

As amber matures over the years, more polymerization takes place as well as isomerization reactions, crosslinking and cyclization.

1.4.1.5 Structure and Nomenclature

- The principal method of polymerizing monomers by the chain kinetic scheme involves the opening of double bonds to form a linear molecule.
- In a reacting mixture, monomer, fully reacted polymer, and only a small amount of rapidly reacting species are present. Once the polymer terminates, it is "dead" and cannot react further by the synthesis scheme outlined previously.

- → Names of polymers
- Polymers are named by rules laid out by the IUPAC Nomenclature Committee (8,9). [Discussed at end: Appendix]

- For many simple polymers, the **source-based name** utilizes the monomer name prefixed by "poly."
- If the monomer name has two or more words, parentheses are placed around the monomer name. Thus, in the above, the monomer “ethyl acrylate” is polymerized to make poly(ethyl acrylate).

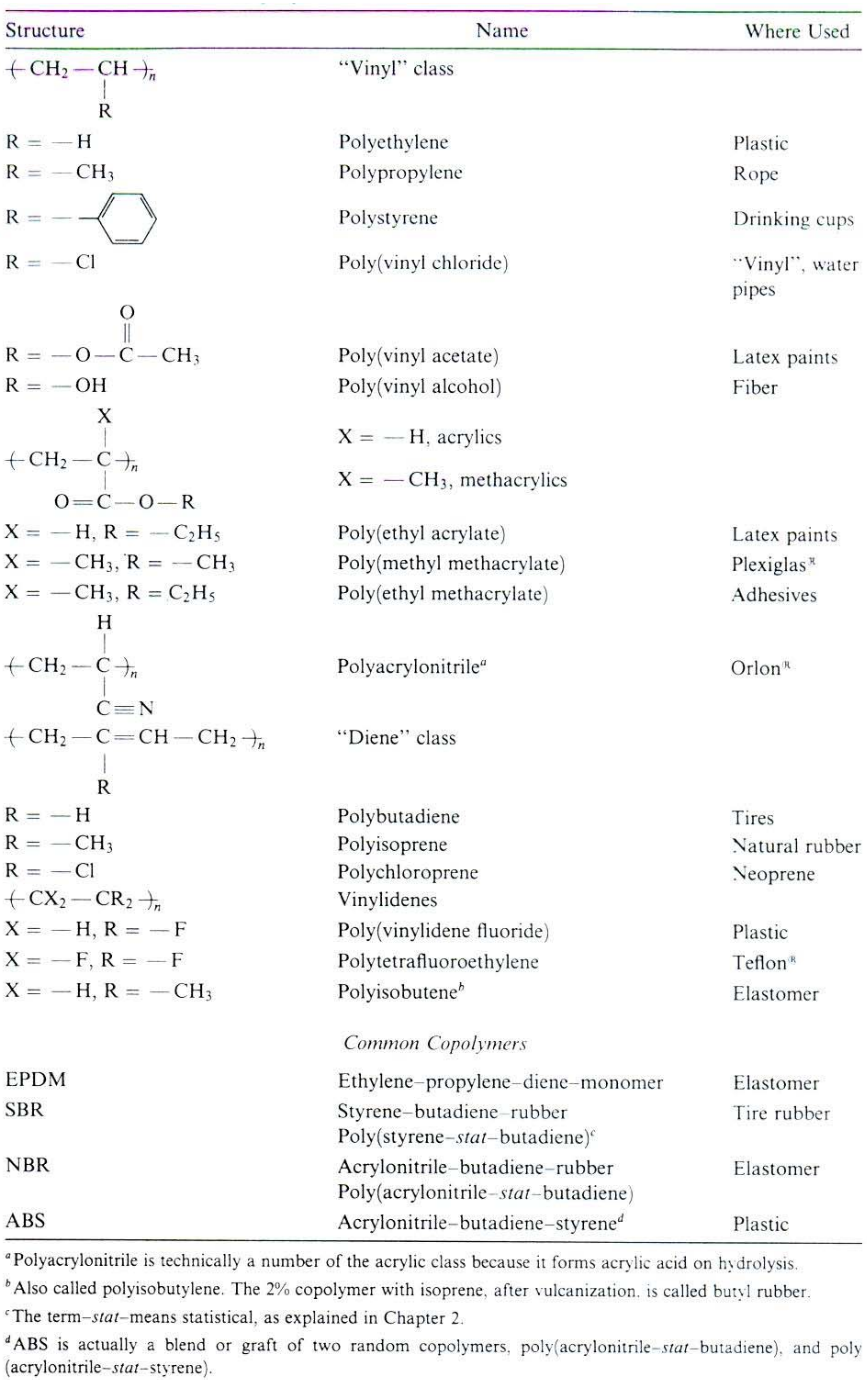
- **Table 1.4** provides a selected list of common **chain polymer structures** and names along with comments as to how the polymers are used.
- The "vinyl" monomers are characterized by the general structure CH_2 = CHR, where R represents any side group. One of the best-known **vinyl polymers** is poly(vinyl chloride), where R is -Cl.

- Polyethylene and polypropylene are the major members of the class of polymers known as **polyolefins**; see Section 14.1. The term ***olefin*** derives from the double-bond **characteristic of the alkene series**.

- The **diene monomer** has the general structure $CH_2=CR-CH=CH_2$, where on polymerization one of the double bonds forms the chain bonds, and the other goes to the central position. **The vinylidenes have two groups on one carbon.**
- **Table 1.4** also lists some common copolymers, which are formed by reacting two or more monomers together.

Note→: A slight **dichotomy** (contradiction) exists in the writing of vinyl polymer structure. From a correct point of view, **poly(vinyl chloride)** should be written **$-(CHCl-CH_2)-_n$**. However, from a synthesis point of view, the structure is written **$-(CH_2-CHCl)-_n$**, because **the free radical is borne on the pendant moiety carbon**.

Thus both forms appear in the literature.



Structure	Name	Where Used
$\left(CH_2-\underset{\underset{R}{\vert}}{CH}\right)_n$	"Vinyl" class	
R = —H	Polyethylene	Plastic
R = —CH_3	Polypropylene	Rope
R = —	Polystyrene	Drinking cups
R = —Cl	Poly(vinyl chloride)	"Vinyl", water pipes
$R = -O-\overset{\overset{O}{\Vert}}{C}-CH_3$	Poly(vinyl acetate)	Latex paints
R = —OH	Poly(vinyl alcohol)	Fiber
$\left(CH_2-\underset{\underset{O=C-O-R}{\vert}}{\overset{\overset{X}{\vert}}{C}}\right)_n$	X = —H, acrylics X = —CH_3, methacrylics	
X = —H, R = —C_2H_5	Poly(ethyl acrylate)	Latex paints
X = —CH_3, R = —CH_3	Poly(methyl methacrylate)	Plexiglas®
X = —CH_3, R = C_2H_5	Poly(ethyl methacrylate)	Adhesives
$\left(CH_2-\underset{\underset{C\equiv N}{\vert}}{\overset{\overset{H}{\vert}}{C}}\right)_n$	Polyacrylonitrile[a]	Orlon®
$\left(CH_2-\underset{\underset{R}{\vert}}{C}=CH-CH_2\right)_n$	"Diene" class	
R = —H	Polybutadiene	Tires
R = —CH_3	Polyisoprene	Natural rubber
R = —Cl	Polychloroprene	Neoprene
$\left(CX_2-CR_2\right)_n$	Vinylidenes	
X = —H, R = —F	Poly(vinylidene fluoride)	Plastic
X = —F, R = —F	Polytetrafluoroethylene	Teflon®
X = —H, R = —CH_3	Polyisobutene[b]	Elastomer
	Common Copolymers	
EPDM	Ethylene–propylene–diene–monomer	Elastomer
SBR	Styrene–butadiene–rubber Poly(styrene–*stat*–butadiene)[c]	Tire rubber
NBR	Acrylonitrile–butadiene–rubber Poly(acrylonitrile–*stat*–butadiene)	Elastomer
ABS	Acrylonitrile–butadiene–styrene[d]	Plastic

[a] Polyacrylonitrile is technically a number of the acrylic class because it forms acrylic acid on hydrolysis.

[b] Also called polyisobutylene. The 2% copolymer with isoprene, after vulcanization, is called butyl rubber.

[c] The term–*stat*–means statistical, as explained in Chapter 2.

[d] ABS is actually a blend or graft of two random copolymers, poly(acrylonitrile–*stat*–butadiene), and poly (acrylonitrile–*stat*–styrene).

Table 1.4
Selected **chain polymer** structures and nomenclature

Recycling – Code number/identification letters:

- Today, recycling of plastics has become paramount in preserving the environment.

- On the bottom of plastic bottles and other plastic items is an identification number and letters; see **Table 1.5**.

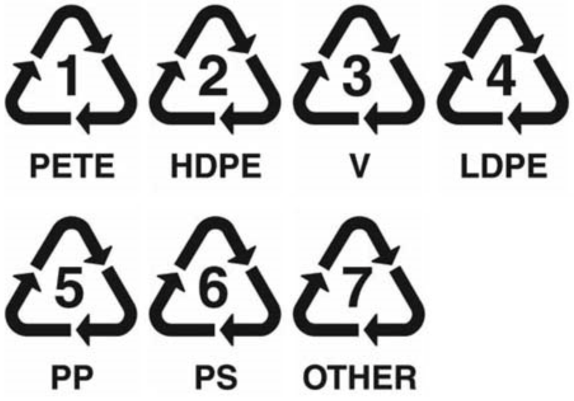
  This information serves to help in separation of the plastics prior to recycling. Observation of the properties of the plastic such as modulus, together with the identification, will help the student understand the kinds and properties of the plastics in common service.

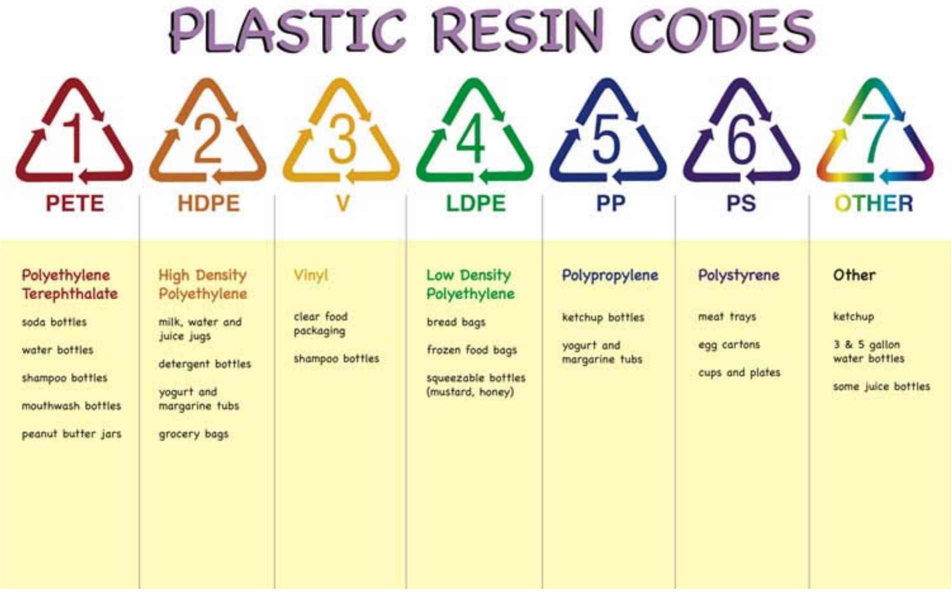
Table 1.5 The plastics identification code [for recycling]

Code	Letter I.D.	Polymer Name
♳	PETE	Poly(ethylene terephthalate)
♴	HDPE	High-density polyethylene
♵	V	Poly(vinyl chloride)
♶	LDPE	Low-density polyethylene
♷	PP	Polypropylene
♸	PS	Polystyrene
♹	Other	Different polymers

Source: From the *Plastic Container Code System*, The Plastic Bottle Information Bureau, Washington, DC.

PLLA




PLASTIC RESIN CODES

1 PETE	2 HDPE	3 V	4 LDPE	5 PP	6 PS	7 OTHER
Polyethylene Terephthalate	High Density Polyethylene	Vinyl	Low Density Polyethylene	Polypropylene	Polystyrene	Other
soda bottles water bottles shampoo bottles mouthwash bottles peanut butter jars	milk, water and juice jugs detergent bottles yogurt and margarine tubs grocery bags	clear food packaging shampoo bottles	bread bags frozen food bags squeezable bottles (mustard, honey)	ketchup bottles yogurt and margarine tubs	meat trays egg cartons cups and plates	ketchup 3 & 5 gallon water bottles some juice bottles

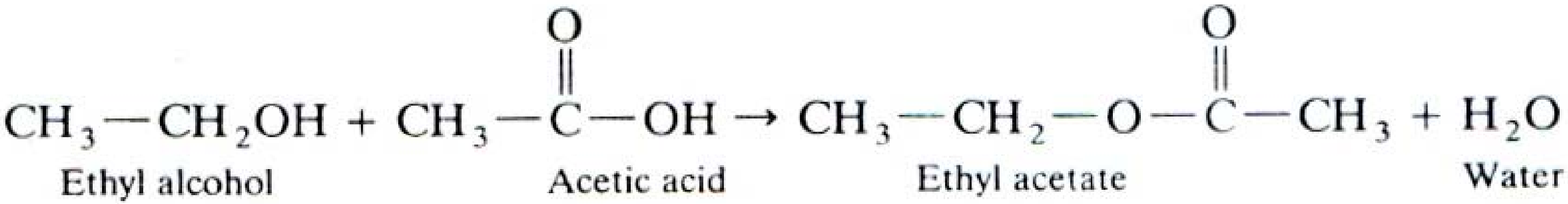
Type of Plastic	Examples of What is Acceptable for Recycling	NOT Acceptable for Recycling	It Gets Made Into…
1 **PET** **polyethylene terephalate** *It's tough and shatterproof.*	Peanut butter jars. Narrow-neck containers, such as for detergents, mouth wash, salad dressing, vitamins, soda and water bottles.	Thin, brittle plastics and "clamshell" packaging—often used to hold items such as strawberries, baked goods such as muffins, or salad bar meal containers.	Bottles, carpeting, tennis balls, insulation for jackets, t-shirts, paint brushes.
2 **HDPE** **high density polyethylene** *It's flexible and often translucent.*	Milk and water jugs, juice bottles, dairy tubs such as whipped topping or sour cream, liquid detergent bottles, medicine bottles, kitty litter jugs, plastic grocery bags.	Materials made from Tyvek, such as envelopes and protective gear.	Plastic lumber, detergent and bleach bottles, trash cans, buckets, toys, traffic barriers, fly swatters.
3 **PVC** **polyvinyl chloride** *It's tough and chemical resistant.*	Bottles for shampoo, cooking oil, salad dressing.	PVC pipes, lawn furniture or objects too large to fit in a recycling cart (these items can be brought to the specially designated recycling bin at the DSWM facilities, 9031 Reichs Ford Rd.)	Floor mats, mud flaps, pipes, hoses, computer and electric cord wraps.
4 **LDPE** **low density polyethylene** *It's flexible and tough.*	Food storage containers, dairy container lids, bags newspapers are delivered in, dry cleaning bags.	Bags without a plastic identification number printed on them.	Garbage can liners, frisbees, plastic lumber, lawn furniture, toys.
5 **PP** **polypropylene** *It's chemical and heat resistant.*	Medicine bottles, deli containers, yogurt containers, rigid/reuseable plastic cups, nursery plant packs and pots.	Thin, brittle #5 plastics, such as disposable plates and drinking cups. Polypropylene fabrics.	Brooms, lawn mower wheels, ice scrapers, paint buckets, toothbrushes. Spun fiber fabrics and filling for coats, sleeping bags and blankets.
6 **PS** **polystyrene** *It's brittle and see-through OR soft opaque foam.*	Dairy containers, medicine and vitamin bottles, flower pots.	Disposable foam hot/cold beverage cups, carry-out containers, foam egg cartons, disposable plates, packing peanuts, *anything* styrofoam.	Building insulation, flower pots, CD cases and sleeves, rulers, trash cans, food service trays.
7 ***OTHER*** **other plastics**	Bottles such as for ketchup, syrup, window cleaner, 5-gallon water coolers.	Objects too large to fit in a recycling cart, and in general, objects without an identification code imprinted on them.	Street signs, pens, concrete supports, ice scrapers.

1.4.2 Step Polymerization

p. 11

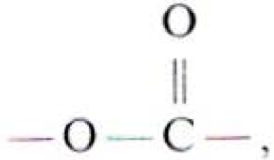
1.4.2.1 A Polyester Condensation Reaction

- The second important kinetic scheme is **step polymerization**. As an example of a step polymerization, the synthesis of a polyester is given. The general reaction to form esters starts with an acid and an alcohol:



$$CH_3-CH_2OH + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH \rightarrow CH_3-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H_2O \quad (1.12)$$

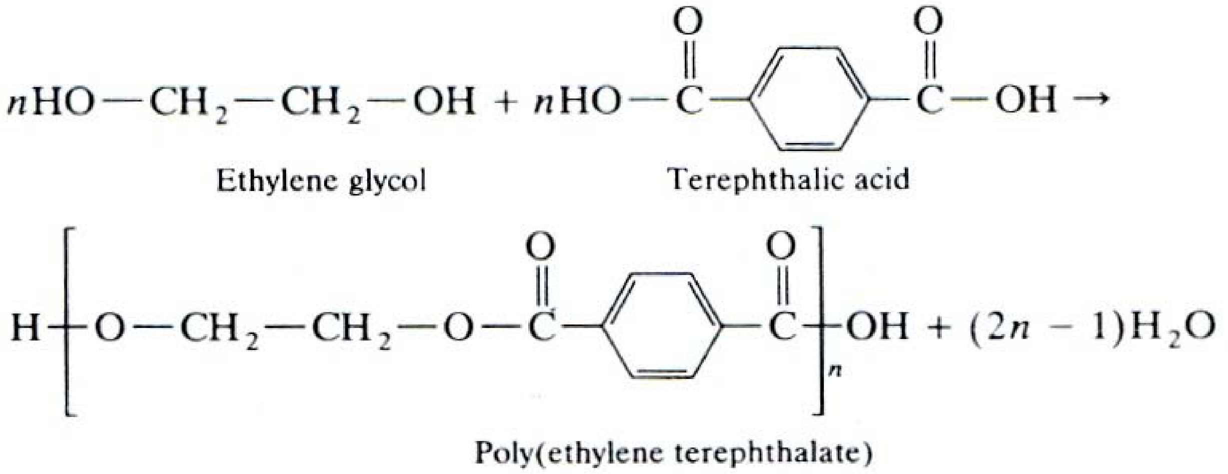
Ethyl alcohol   Acetic acid   Ethyl acetate   Water



where the ester group is $-O-\overset{\overset{\displaystyle O}{\|}}{C}-$, and water is eliminated.

Cont/d

- The chemicals above cannot form a polyester because they have only one functional group each. When the two reactants each have **bifunctionality**, a linear polymer is formed:

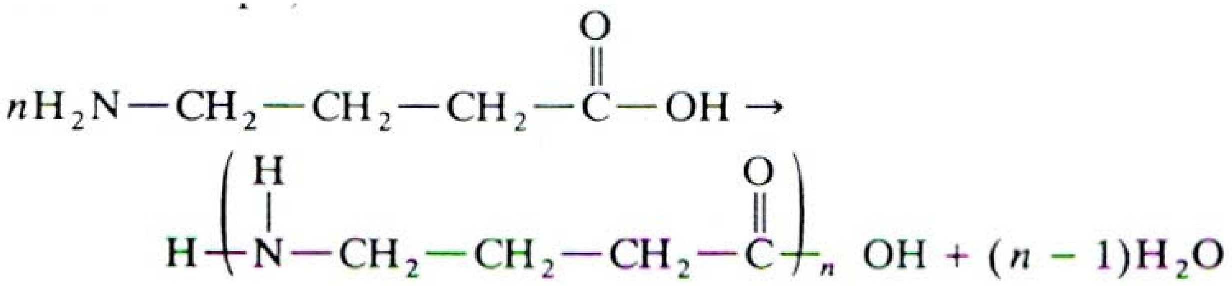


(1.13)

- In the stepwise reaction scheme, **monomers, dimers, trimers, and so on, may all react together**. All that is required is that the appropriate functional groups meet in space. Thus the molecular weight slowly climbs as the small molecule water is eliminated.
- Industrially, -CO-OH is replaced by -CO-O-CH$_3$. Then, the reaction is an **ester interchange**, releasing **methanol**.

- **Polymers by step polymerization**: Poly(ethylene terephthalate) [PET] is widely known as the fiber “**Dacron**". It is highly crystalline, with a melting temperature of about +265^{o}C.

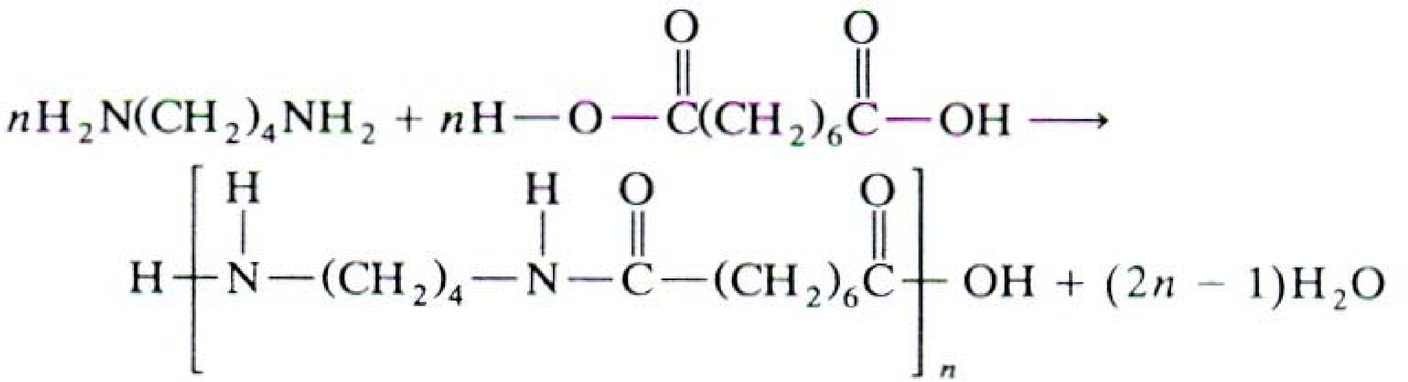
- Another well-known series of polymers made by **step polymerization reactions** is the **polyamides**, known widely as the **nylons**.
- In fact there are **two series of nylons**. **In the first series, the monomer has an amine at one end of the molecule and a carboxyl at the other.** For example,



$$nH_2N-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH \rightarrow H\left(\overset{H}{\overset{|}{N}}-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}\right)_n OH + (n-1)H_2O \qquad (1.14)$$

- which is known as **nylon 4**. The number 4 indicates the number of carbon atoms in the mer.

- **In the second series, a dicarboxylic acid is reacted with a diamine**:



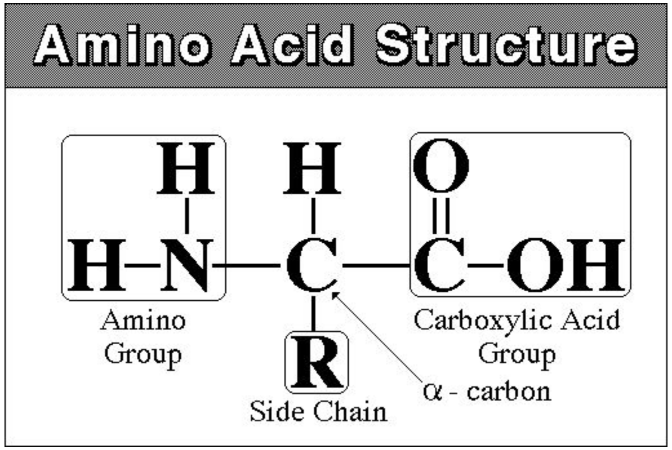
$$nH_2N(CH_2)_4NH_2 + nH-O-\overset{O}{\overset{\|}{C}}(CH_2)_6\overset{O}{\overset{\|}{C}}-OH \longrightarrow H\left[-\overset{H}{\overset{|}{N}}-(CH_2)_4-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_6\overset{O}{\overset{\|}{C}}-\right]_n OH + (2n-1)H_2O \qquad (1.15)$$

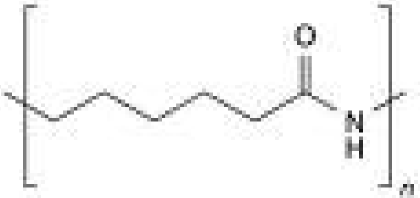
which is named **nylon 48**. Note that the **amine carbon number is written first**, and the **acid carbon number second**. For reaction purposes, **acyl chlorides** (-COCl) are frequently substituted for the **carboxyl groups**. [To release Cl_2 or HCl gas instead of H_2O vapor)

An excellent demonstration experiment is described by Morgan and Kwolek (10), called the nylon rope trick. [ref. 10: J. Chem. Ed, 36, 182, 530 (1959)] – students should search for references.

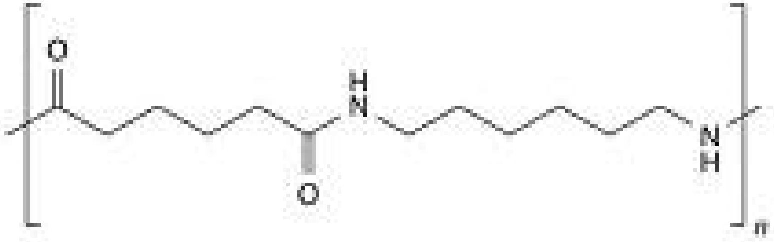
Alpha-amino acids – amine on “alpha-carbon” [胺基酸]

Note: “alpha” means both the acid and amino groups are attached to the same carbon.
There are “alpha”, “beta”, and “gamma” amino acids.

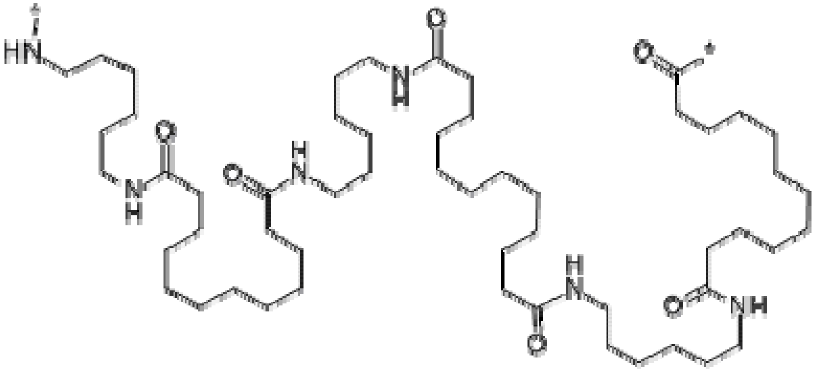




Nylon 6



Nylon 6,6

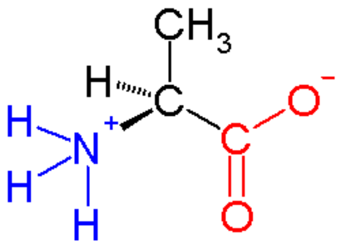


Synthetic polymers:
Nylon-12, nylon-6, nylon 6,6, etc.,
are also produced from “amino acids”

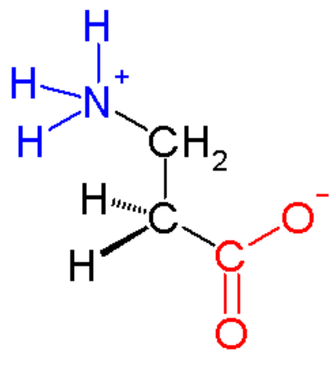
There are alpha- (α-), beta- (β-), gamma- (γ-), or delta- (δ-) amino acids

β-peptides consist of "**β amino acids**", which have their amino group bonded to the β carbon rather than the α carbon as in the 20 standard biological amino acids.

The only common naturally occurring β amino acid is "β-alanine".

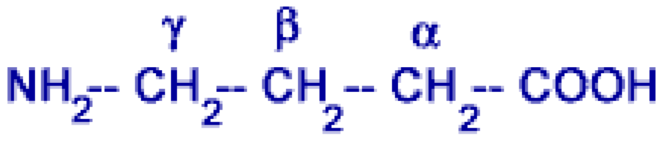


L-α-alanine



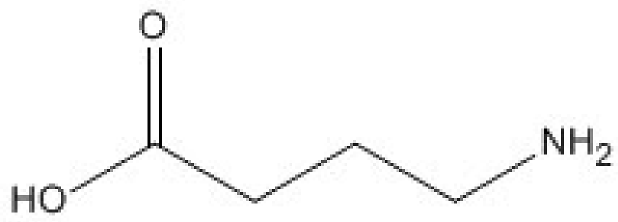
β-alanine

gamma amino acid

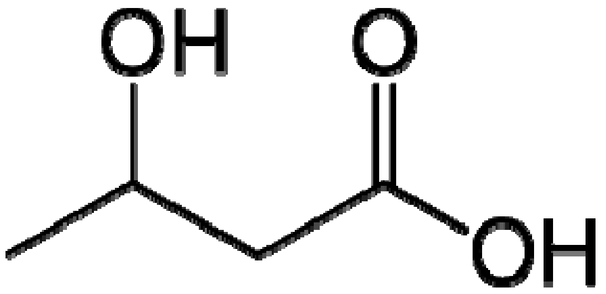


$$\overset{}{NH_2}\text{--}\overset{\gamma}{CH_2}\text{--}\overset{\beta}{CH_2}\text{--}\overset{\alpha}{CH_2}\text{--}COOH$$

γ – Amino acid



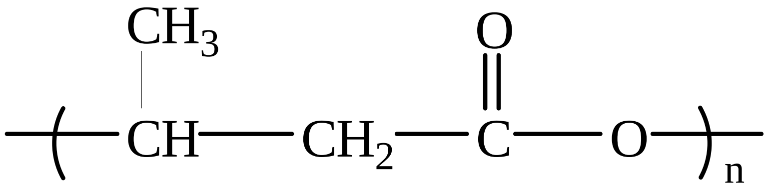
gamma amino butyric acid



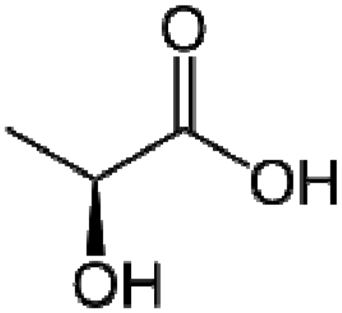
"β-hydroxyl butyric acid". –
Or "**3-hydroxy butyric acid**"
Monomer for "PHB".

Note "-OH" is on the **beta-carbon** position.

Poly(beta-hydroxyl butyric acid) (PHB)
Or Poly(3-hydroxyl butyric acid)


$-\!\!\left(\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-O\right)_n$

乳酸（IUPAC學名：2-羥基丙酸）

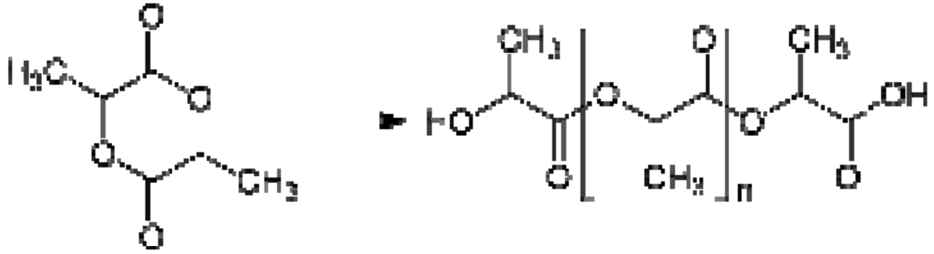


Also called: "α-羥酸"
[α-hydroxy acid] Vs.

"α-胺基酸" [a-amino acid]

"Lactic acid". – Monomer for "PLA"
There are L- or D-form.

Note "-OH" is on the **alpha-carbon** position.
But "alpha" is omitted as there is only one carbon (except for the function acid groups)



1.4.2.2 Stepwise polymers Nomenclature and Structures

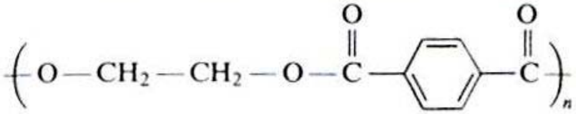
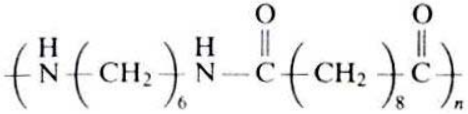
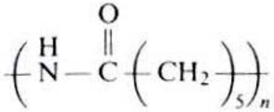
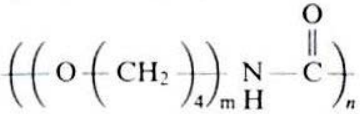
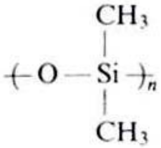
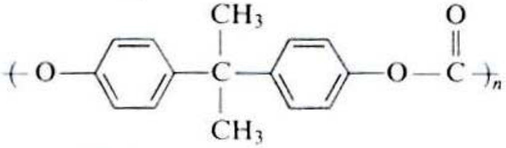
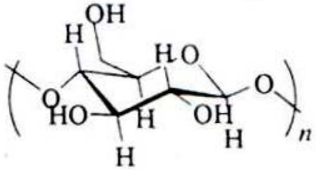
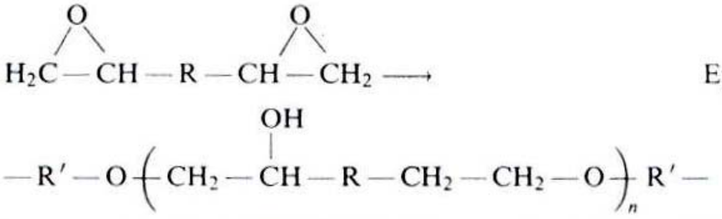
- **Table 1.6** names some of the more important stepwise polymers.
- The **polyesters** have already been mentioned.
- The **nylons** are known technically as **polyamides**. There are two important sub-series of nylons, where amine and the carboxylic acid are on different monomer molecules (thus requiring both monomers to make the polymer) or one each on the ends of the same monomer molecule. These are numbered by the number of carbons present in the monomer species.

It must be mentioned that the proteins are also polyamides.

- Other classes of polymers mentioned in **Table 1.6** include the **polyurethanes**, widely used as **elastomers**; the **silicones**, also elastomeric;

and the **cellulosics** (of celluloses), used in fibers and plastics.

Cellulose is a natural product.

Structure[a]	Name	Where Known
	Poly(ethylene terephthalate)	Dacron®
 $\left(\overset{H}{N}\left(CH_2\right)_6\overset{H}{N}-\overset{O}{\overset{\Vert}{C}}\left(CH_2\right)_8\overset{O}{\overset{\Vert}{C}}\right)_n$	Poly(hexamethylene sebacamide)	Polyamide 610[b]
 $\left(\overset{H}{N}-\overset{O}{\overset{\Vert}{C}}\left(CH_2\right)_5\right)_n$	Polycaprolactam	Polyamide 6
$\left(O\left(CH_2\right)_4\right)_n$	Polytetrahydrofuran	Polyether
 $\left(\left(O\left(CH_2\right)_4\right)_m\underset{H}{N}-\overset{O}{\overset{\Vert}{C}}\right)_n$	Polyurethane[c]	Spandex Lycra®
 $\left(O-\overset{CH_3}{\underset{CH_3}{Si}}\right)_n$	Poly(dimethyl siloxane)	Silicone rubber
	Polycarbonate	Lexan®
	Cellulose	Cotton
	Epoxy resins	Epon®

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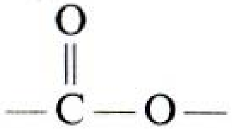
[a] Some people see the mer structure in the third row more clearly with

Table 1.6
Selected stepwise structure and nomenclature

Step-wise polymers

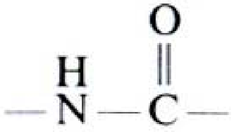
- To summarize the material in Table 1.6, the major **stepwise polymer** classes contain the following identifying groups:

Polyesters



$-\overset{\overset{O}{\|}}{C}-O-$

Polyamides

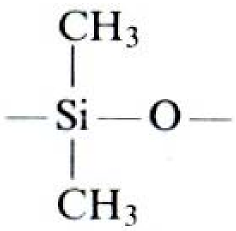


$-\overset{H}{N}-\overset{\overset{O}{\|}}{C}-$

Polyurethanes

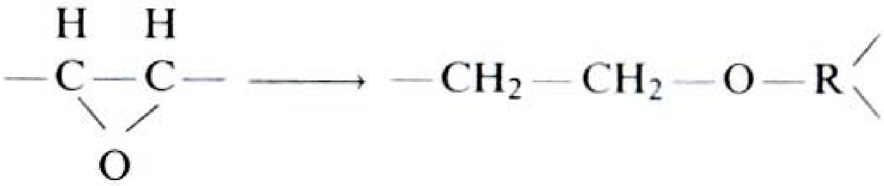
$-\overset{H}{N}-\overset{\overset{O}{\|}}{C}-O-$

Silicones



$-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-$

Epoxy resins



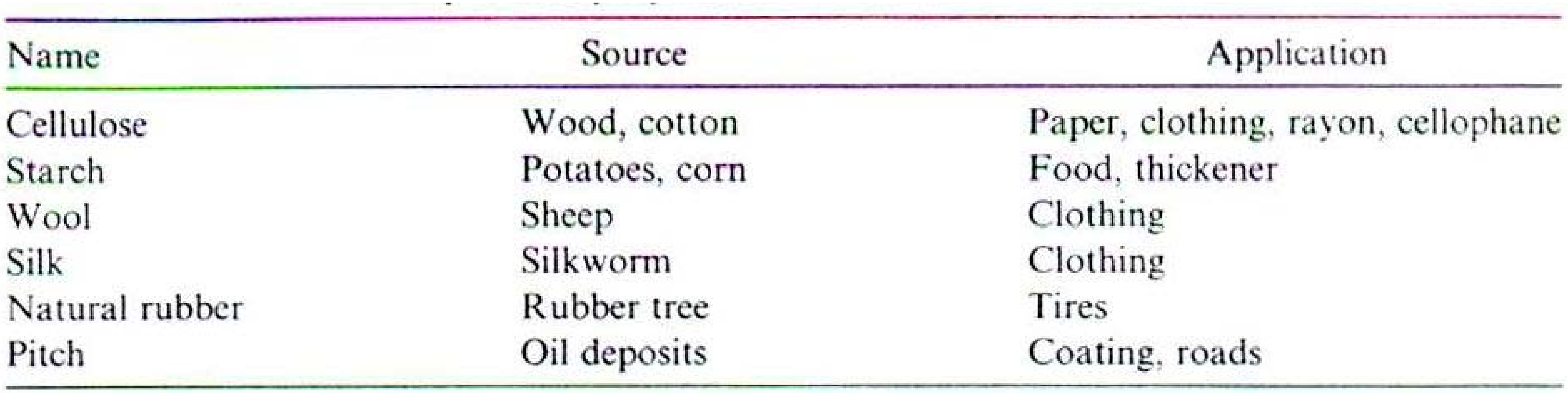
$-\underset{\diagdown\,O\,\diagup}{\overset{H}{C}-\overset{H}{C}}- \longrightarrow -CH_2-CH_2-O-R<$

Polyethers $-O-$

1.4.2.3 **Natural Product Polymers**

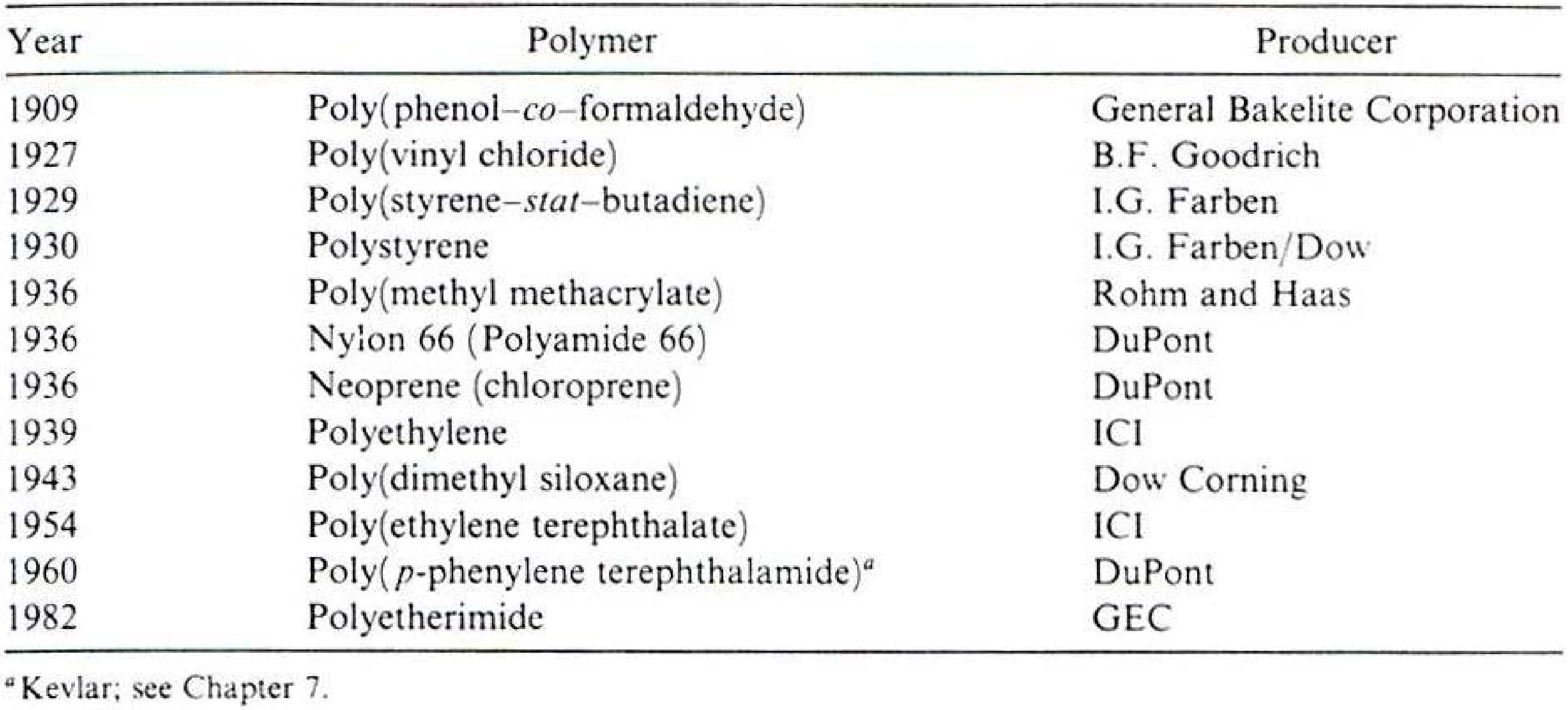
- **Living organisms make many polymers, nature's best.**
- **Most such natural polymers strongly resemble step-polymerized materials**. However, living organisms make their polymers enzymatically, the structure ultimately being controlled by **DNA, itself a polymer [double-spiral protein]**.
- Some of the more important commercial **natural polymers** are shown in **Table 1.7**. People sometimes refer to these polymers as **natural products** or **renewable resources**.
- Wool and silk are both **proteins**. All proteins are actually "**copolymers of polyamide-2**" (or nylon-2, old terminology). [Monomers: amino acids with 2 carbons]
- As made by plants and animals, however, the protein copolymers are **highly ordered**, and they have **monodisperse molecular weights**, meaning that all the chains have the same molecular weights. (For proteins only, not for cellulose – which is polydispersed of different Mw's)

Table 1.7 Some natural product polymers



Name	Source	Application
Cellulose	Wood, cotton	Paper, clothing, rayon, cellophane
Starch	Potatoes, corn	Food, thickener
Wool	Sheep	Clothing
Silk	Silkworm	Clothing
Natural rubber	Rubber tree	Tires
Pitch	Oil deposits	Coating, roads

Table 1.8 Commercialization dates of selected synthetic polymers(20)



Year	Polymer	Producer
1909	Poly(phenol–*co*–formaldehyde)	General Bakelite Corporation
1927	Poly(vinyl chloride)	B.F. Goodrich
1929	Poly(styrene–*stat*–butadiene)	I.G. Farben
1930	Polystyrene	I.G. Farben/Dow
1936	Poly(methyl methacrylate)	Rohm and Haas
1936	Nylon 66 (Polyamide 66)	DuPont
1936	Neoprene (chloroprene)	DuPont
1939	Polyethylene	ICI
1943	Poly(dimethyl siloxane)	Dow Corning
1954	Poly(ethylene terephthalate)	ICI
1960	Poly(*p*-phenylene terephthalamide)[a]	DuPont
1982	Polyetherimide	GEC

[a] Kevlar; see Chapter 7.

Cont’d

- **Cellulose and starch** are both **polysaccharides**, being composed of chains of glucose-based rings but bonded differently. Their structures are discussed further in Appendix 2.1 (end of Chap 2). [Note: saccharides = carbohydrates, or sugars] (**Latin**: saccharum, sugar)

- **Natural rubber**, the hydrocarbon **polyisoprene**, more closely resembles **chain polymerized materials**. → In fact, synthetic polyisoprene can be made either by **free radical** polymerization or **anionic** polymerization.
- **The natural and synthetic products compete commercially with each other**. [→in rubber tires, and all rubber products]

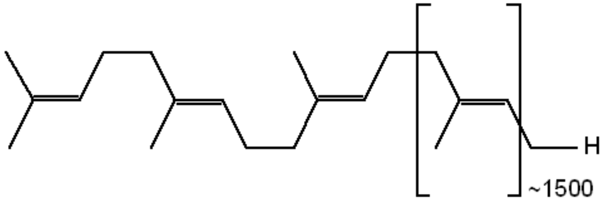
  [isoprene, $CH_2=C(CH_3)-\mathbf{CH}=CH_2$] (error corrected)

  [Note: Property: natural rubbers win. Cost: synthetic rubbers win.]

- **Pitch (a viscoelastic polymer)**, a decomposition product, usually contains a variety of aliphatic and aromatic hydrocarbons, some of very high molecular weights. *[Used in highway pavement or water sealants]*

Gutta Percha – an isomer of natural rubber

- Gutta Percha is a natural polymer, chemically the same as natural rubber (cis-form), however, it has a different molecular shape, giving it different properties.
- Chemically, gutta-percha is a polyterpene, a polymer of isoprene, i.e., polyisoprene, or specifically (trans-1,4-polyisoprene).



PS: Natural rubber (cis) vs. gutta percha (trans)

- **Natural rubber** Latex is a natural polymer of isoprene (most often **cis-1,4-polyisoprene**) – with a molecular weight of 100,000 to 1,000,000. Typically, a small percentage (up to 5% of dry mass) of other materials, such as proteins, fatty acids, resins and inorganic materials (salts) are found in natural rubber.
- **Polyisoprene** is also created synthetically, producing what is sometimes referred to as "synthetic natural rubber".
- Some natural rubber sources called gutta-percha are composed of trans-1,4-polyisoprene, a structural isomer which has similar, but not identical, properties. [Note: cis vs. trans configurations will be discussed in Chap. 2]
- Natural rubber is an elastomer and a thermoplastic. →However, it should be noted that once the rubber is vulcanized, it will turn into a thermoset.
- ***Most rubber in everyday use is vulcanized to a point where it shares properties of both; i.e., if it is heated, it is degraded but not destroyed (melted).***

1.5 CROSS-LINKING, **PLASTICIZERS, AND FILLERS**

- The above provides a brief introduction to simple homopolymers, as made **pure**. Only a few of these are finally sold as "**pure**" polymers, such as polystyrene drinking cups and polyethylene films.

- Much more often, polymers are sold with various **additives**. In order that the student may better recognize the polymers, the most important additives are briefly discussed in this chapter.

- Plasticizers are small molecules added to soften a polymer by lowering its glass transition temperature or reducing its crystallinity or melting temperature. The most widely plasticized polymer is **poly(vinyl chloride).** [The distinctive odor of new "vinyl" shower curtains is caused by the plasticizer, for example.]

- **Fillers** may be of two types, reinforcing and nonreinforcing. Common reinforcing fillers are **the silicas and carbon blacks**. The latter are most widely used in automotive tires to improve wear characteristics such as abrasion resistance.
- Nonreinforcing fillers, such as calcium carbonate, may provide color or opacity or may merely lower the price of the final product.

Cross-linking

- On heating, linear polymers flow and are termed thermoplastics.
- To prevent flow, polymers are sometimes cross-linked (·):

(1.16)

- The cross-linking of rubber with **sulfur** is called **vulcanization**. Cross-linking bonds the chains together to form a network. The resulting product is called a **thermoset**, because it does not flow on heating.

[Note: → Some proteins can also be crosslinked by sulfur.]

1.6 THE MACROMOLECULAR **HYPOTHESIS** – 90 years ago

- **In the nineteenth century, the structure of polymers was almost entirely unknown.** The Germans called it ***Schmierenchemie***, meaning **grease chemistry** (11), but a better translation might be "the **gunk** (greasy material) at the bottom of the flask," that portion of an organic reaction that did not result in characterizable products.
- In the nineteenth century and early twentieth century the field polymers and the field of **colloids** were considered integral parts of the same field.

- **Wolfgang Ostwald** declared in 1917 (12):

  All those sticky, mucilaginous [French: sticky], resinous, tarry masses which refuse to crystallize, and which are the abomination [detest, dislike] of the normal organic chemist; those substances which he carefully sets toward the back of his cupboard ... , just these are the substances which are the delight of the **colloid chemist**. [translation from German]

Colloids → Polymers [90 years ago]

- In 1920 **Herman Staudinger** (13,14) enunciated the ***Macromolecular Hypothesis***. It states that certain kinds of these **colloids** actually consist of very **long-chained molecules.**
- These came to be called **polymers** because many (but not all) were composed of the **same repeating unit**, or 'mer' – so called ""poly"-"mer".

- →**In 1953, Staudinger won the Nobel prize in chemistry for his discoveries in the chemistry of macromolecular substances (15).**
- The **Macromolecular Hypothesis** is the origin of modem polymer science, leading to our current understanding of how and why such materials as plastics and rubber have the properties they do.

1.7 HISTORICAL DEVELOPMENT OF INDUSTRIAL POLYMERS

- Like most other technological developments, **polymers were first used on an empirical basis, with only a very incomplete understanding of the relationships between structure and properties.**
- The first polymers used were **natural products** that date back to antiquity, including wood, leather, cotton, various grasses for fibers, papermaking, and construction, wool, and protein animal products boiled down to make glues and related material.
- Then came several **semisynthetic polymers**, which were natural polymers modified in some way. One of the first to attain commercial importance was **cellulose nitrate** plasticized with camphor [樟腦$C_{10}H_{16}O$], popular around 1885 for stiff collars and cuffs as celluloid, later most notably used in Thomas Edison's motion picture film (11). Cellulose nitrates were also sold as lacquers, used to coat wooden staircases, and so on.

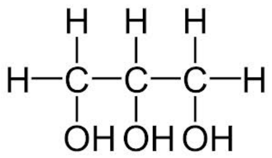
- The problem was the terrible fire hazard existing with the **nitrates**, which were later replaced by the **acetates**.

From natural polymers to synthetic polymers

- Other early polymer materials included Chardonnet‘s **artificial silk [天絲]**, made by regenerating and spinning **cellulose nitrate** solutions, eventually leading to the viscose process for making **rayon** (see Section 6.10) still in use today.

- The **first truly synthetic polymer** was a densely cross-linked material based on the reaction of **phenol and formaldehyde**; see Section 14.2. The product, called **Bakelite** (crosslinked phenolic ether), was manufactured from 1910 onward for applications ranging from electrical appliances to phonograph records [黑膠唱片] (16,17).

- Another early material was the General Electric Company's **Glyptal** (crosslinked polyesters), based on the condensation reaction of **glycerol and phthalic anhydride** (or cross-linked polyester made by polymerising glycerol and phthalic acid) (18), which followed shortly after **Bakelite**.



$$H-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H$$

- However, very little was known about the actual chemical structure of these polymers **until after Staudinger enunciated the Macromolecular Hypothesis in 1920**.

Cont'd

- All of these materials were made on a more or less **empirical basis**; trial and error have been the basis for very many advances in history, including polymers.
- However, in the late 1920s and 1930s, a **DuPont chemist** by the name of **Wallace Carothers** succeeded in establishing the reality of the Macromolecular Hypothesis by bringing the organic structural approach back to the study of polymers, resulting in the discovery of nylon and neoprene.
- Actually **the first polymers that Carothers discovered were polyesters (19).** He reasoned that if the Macromolecular Hypothesis was correct, then if one mixed a molecule with **dihydroxide end groups** with a another molecule with **diacid end groups** and allowed them to react,, a long, linear chain should result if the stoichiometry was one-to-one.

Cont'd

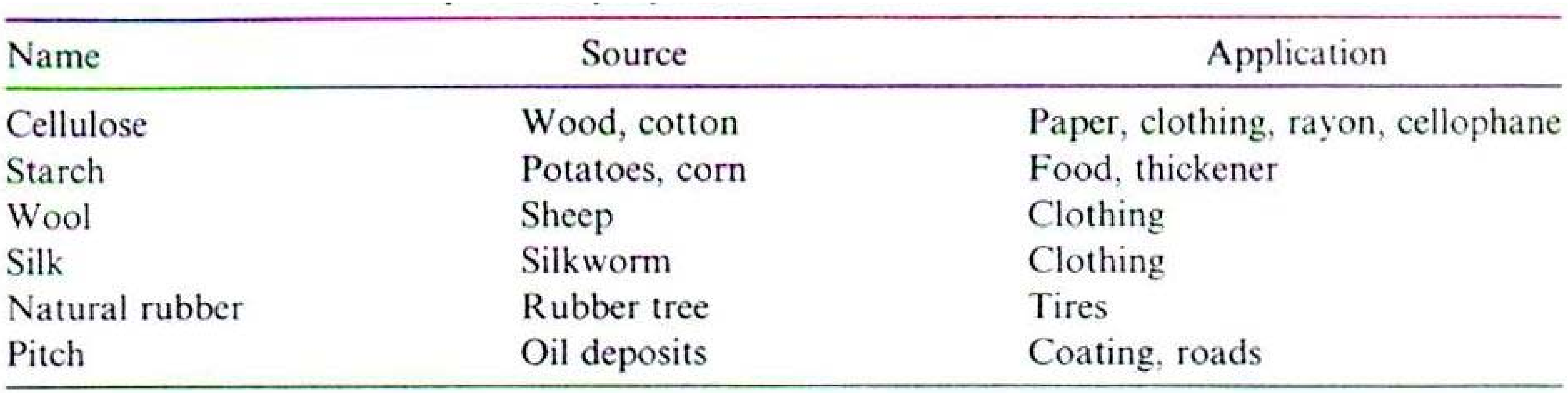
- The problem with the **aliphatic polyesters** made at that time was their low melting point, making them unsuitable for clothing fibers because of hot water washes and ironing.

- When the **ester** (-COO-)groups were replaced with the higher melting **amide** (-CONH-) groups, the **nylon series** was born.

- **Bakelite** was a thermoset; that is, it did not flow after the synthesis was complete (20).

- The first **synthetic thermoplastics**, materials that could flow on heating, were **polyethylene**, **poly(vinyl chloride), poly(styrene-stat-butadiene), polystyrene, and polyamide 66**; see **Table 1.8** (20).
- Other breakthrough polymers have included the very high modulus aromatic polyamides, known as **Kevlar** (see Section 7.4), and a host of high temperature polymers.

Table 1.7 Some natural product polymers



Name	Source	Application
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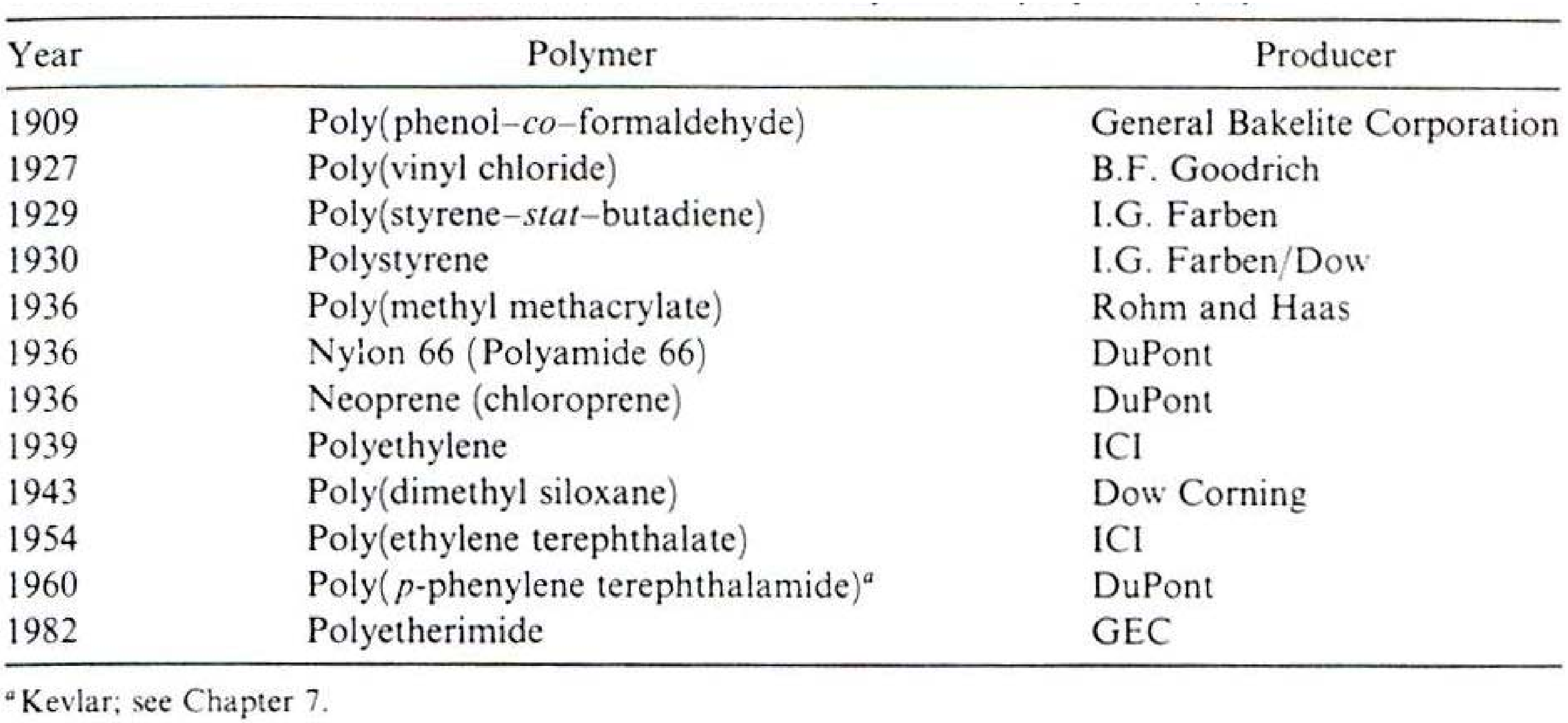

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1939	Polyethylene	ICI
1943	Poly(dimethyl siloxane)	Dow Corning
1954	Poly(ethylene terephthalate)	ICI
1960	Poly(*p*-phenylene terephthalamide)[a]	DuPont
1982	Polyetherimide	GEC

[a] Kevlar; see Chapter 7.

1.8 MOLECULAR ENGINEERING

- The discussion above shows that polymer science is an “**admixture” of pure and applied science**.
- The structure, molecular weight, and shape of the polymer molecule are all closely tied to the physical and mechanical properties of the final material.

- This book emphasizes physical polymer science, the science of the interrelationships between polymer structure and properties. Although much of the material (except the polymer syntheses) is developed in greater detail in the remaining chapters, the intent of this chapter is to provide an overview of the subject and a simple recognition of polymers as encountered in everyday life.

- In addition to the books in the General Reading section, a listing of handbooks and encyclopedias is given at the end of this chapter.

Appendix 1-A

- **APPENDIX 1.1 NAMES FOR POLYMERS**
- The **IUPAC Macromolecular Nomenclature Commission** has developed a systematic nomenclature for polymers (9).
- The Commission recognized, however, that a number of **common polymers** have **semisystematic or trivial** names that are well established by usage.
- For the reader's convenience, the recommended **trivial name** (or the source-based name) of the polymer is given under the polymer structure. and then the structure-based name is given. **For example, the trivial name, polystyrene, is a source-based name, literally "the polymer made from styrene."**
- The **structure-based name**, **poly(1-phenylethylene)** (which is just **polystyrene**), is useful both in addressing people who may not be familiar with the structure of polystyrene and in cases where the polymer is not well known.
- This book uses a **source-based** nomenclature, unless otherwise specified.

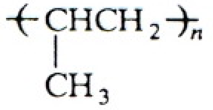
Examples of **IUPAC Macromolecular Nomenclature for some common polymers are given:**

$\left(\mathrm{CH_2CH_2} \right)_n$

polyethylene
poly(methylene)

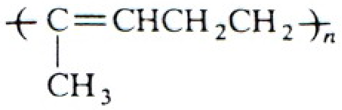
$\left(\mathrm{CH{=}CHCH_2CH_2} \right)_n$

polybutadiene[a]
poly(1-butenylene)



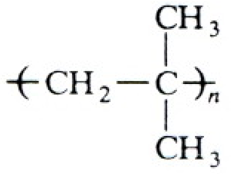
$\left(\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}\mathrm{HCH_2} \right)_n$

polypropylene
poly(1-methylethylene)



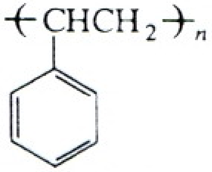
$\left(\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}\mathrm{{=}CHCH_2CH_2} \right)_n$

polyisoprene[b]
poly(1-methyl-1-butenylene)



$\left(\mathrm{CH_2{-}}\overset{\mathrm{CH_3}}{\overset{|}{\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}}} \right)_n$

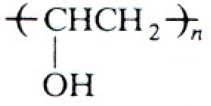
polyisobutylene
poly(1,1-dimethylethylene)



polystyrene
poly(1-phenylethylene)

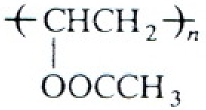
$\left(\underset{\mathrm{CN}}{\underset{|}{\mathrm{C}}}\mathrm{HCH_2} \right)_n$

polyacrylonitrile
poly(1-cyanoethylene)



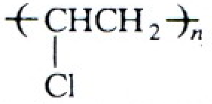
$\left(\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}\mathrm{HCH_2} \right)_n$

poly(vinyl alcohol)
poly(1-hydroxyethylene)



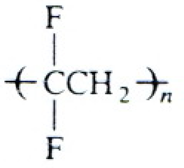
$\left(\underset{\mathrm{OOCCH_3}}{\underset{|}{\mathrm{C}}}\mathrm{HCH_2} \right)_n$

poly(vinyl acetate)
poly(1-acetoxyethylene)



$\left(\underset{\mathrm{Cl}}{\underset{|}{\mathrm{C}}}\mathrm{HCH_2} \right)_n$

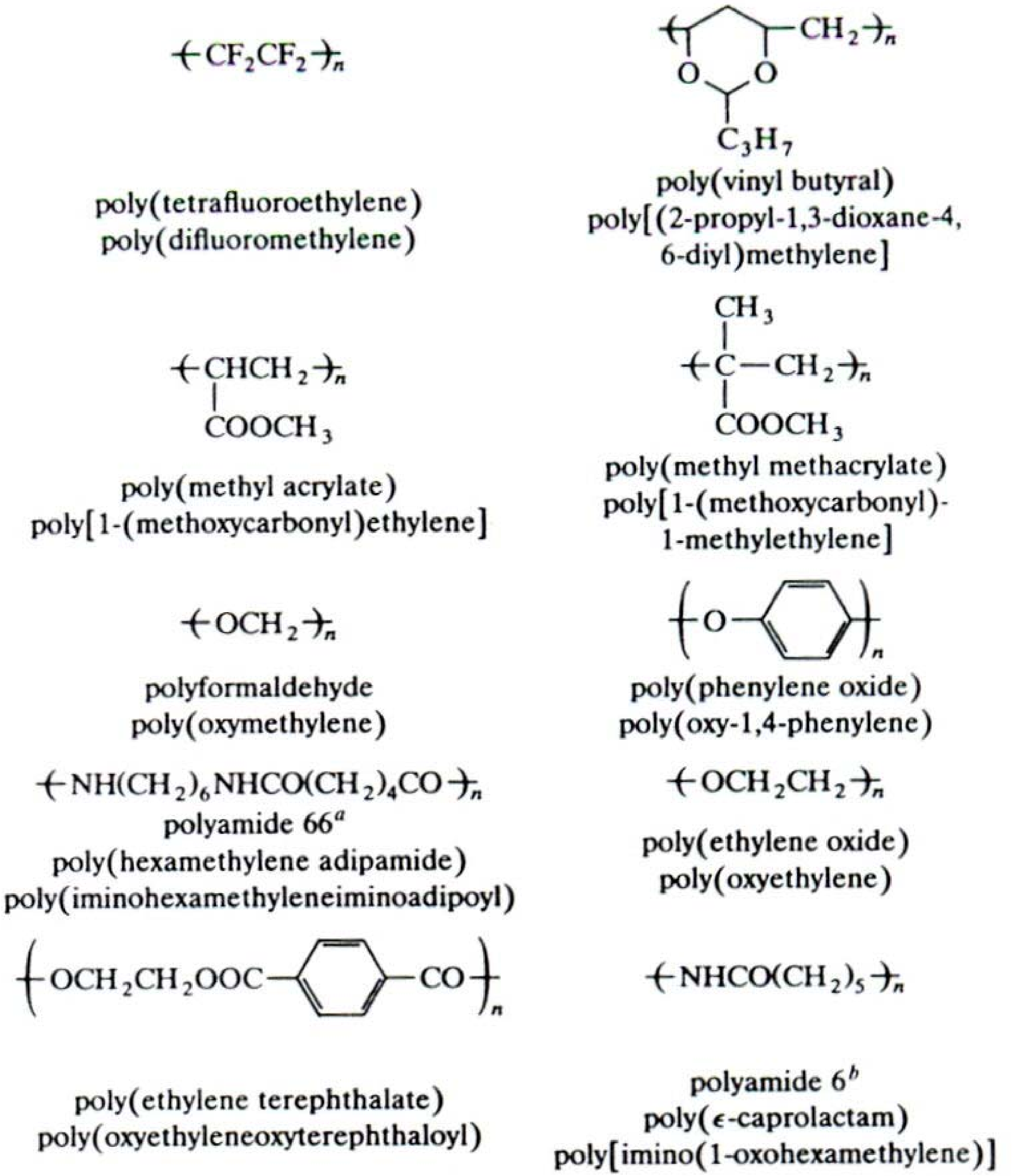
poly(vinyl chloride)
poly(1-chloroethylene)



$\left(\overset{\mathrm{F}}{\overset{|}{\underset{\mathrm{F}}{\underset{|}{\mathrm{C}}}}}\mathrm{CH_2} \right)_n$

poly(vinylidene fluoride)
poly(1,1-difluoroethylene)

Examples of **Common names vs. IUPAC Macromolecular Nomenclature**



$-(\mathrm{CF_2CF_2})-_n$

poly(tetrafluoroethylene)
poly(difluoromethylene)

poly(vinyl butyral)
poly[(2-propyl-1,3-dioxane-4,6-diyl)methylene]

$-(\mathrm{CH(COOCH_3)CH_2})-_n$

poly(methyl acrylate)
poly[1-(methoxycarbonyl)ethylene]

$-(\mathrm{C(CH_3)(COOCH_3)-CH_2})-_n$

poly(methyl methacrylate)
poly[1-(methoxycarbonyl)-1-methylethylene]

$-(\mathrm{OCH_2})-_n$

polyformaldehyde
poly(oxymethylene)

poly(phenylene oxide)
poly(oxy-1,4-phenylene)

$-(\mathrm{NH(CH_2)_6NHCO(CH_2)_4CO})-_n$

polyamide 66[a]
poly(hexamethylene adipamide)
poly(iminohexamethyleneiminoadipoyl)

$-(\mathrm{OCH_2CH_2})-_n$

poly(ethylene oxide)
poly(oxyethylene)

poly(ethylene terephthalate)
poly(oxyethyleneoxyterephthaloyl)

$-(\mathrm{NHCO(CH_2)_5})-_n$

polyamide 6[b]
poly(ϵ-caprolactam)
poly[imino(1-oxohexamethylene)]

'gravity-defying' chain trick

Beads are connected like a polymer

Bead Fountain

珠鍊噴泉

Bead Fountain: A recent puzzle in Physics: The only way to account for the rise is for the chain to receive a kick from the pot from which it is being pulled, say Biggins and his Cambridge colleague Mark Warner.
This challenges not only the explanation given by Mould, but the conventional mathematics of chains.

Rigid discipline in chain of beads (like a rigid polymer): Rather than a flexible string of isolated beads, the chain is more like a series of short, rigid 'rods', say the authors, who publish their results today in Proceedings of the Royal Society A1. In their model, each rod is made up of three beads and two connectors. The size of a rod corresponds to the number of beads it takes to turn a section of chain back on itself by 180 degrees (it takes six).

End of Chap. 1

Home-quiz to be assigned for this chapter…………..

Next class meeting:

Chap 2.

– Chain Structures, Configuration and Conformation in Polymers

[-Ref: Tacticity in Polymers]