

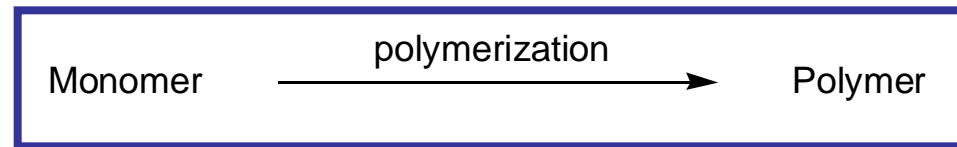
Chapter 1 Basic Principles

1.1 Introduction and Historical Development

Polymer: poly → many mer → many parts
(Greek) “**Macromolecules**”

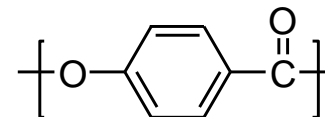
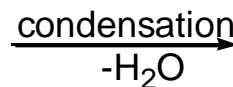
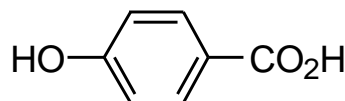
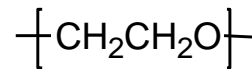
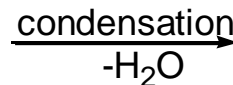
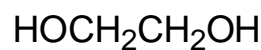
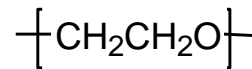
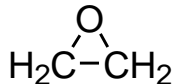
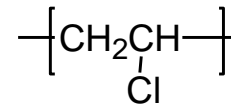
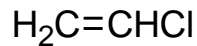
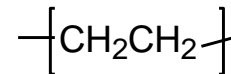
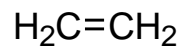
Monomer: mono → single mer → single part

Polymerization:



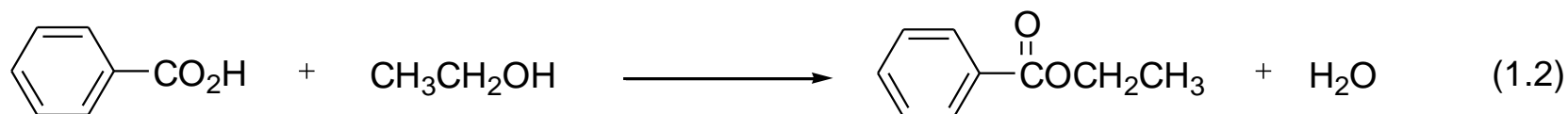
Monomer

Polymer

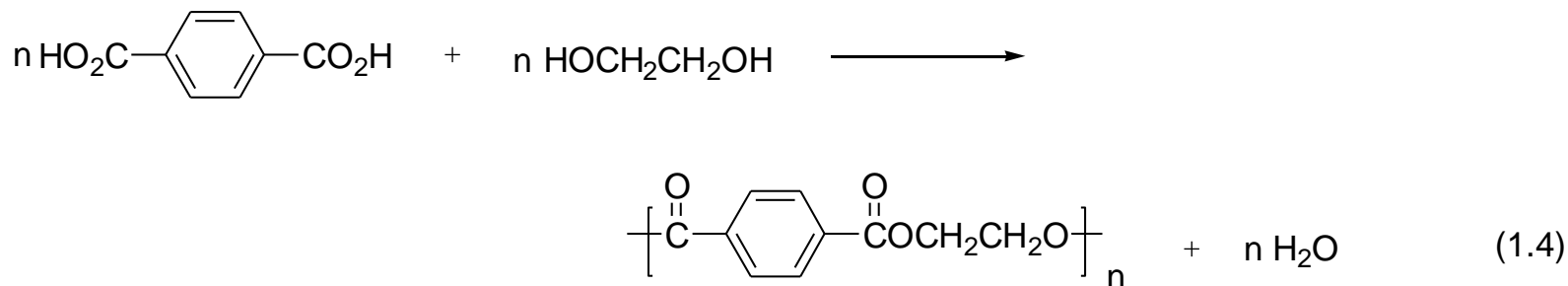
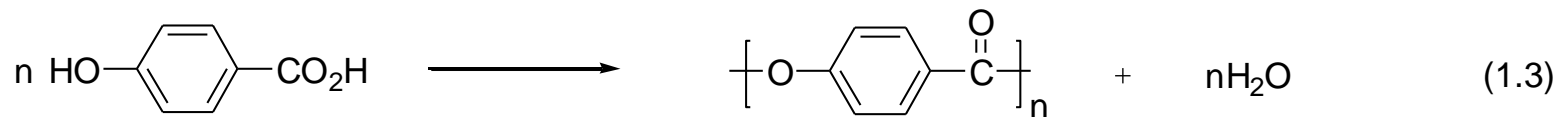


Organic reactions vs Polymerizations

Monofunctional compounds: EtOH, C₆H₅CO₂H



Difunctional compounds: HOCH₂CH₂OH, HOC₆H₄CO₂H



Polymer Historical Events

1833 Berzelius (Swedish)
first time to use the word "polymer"

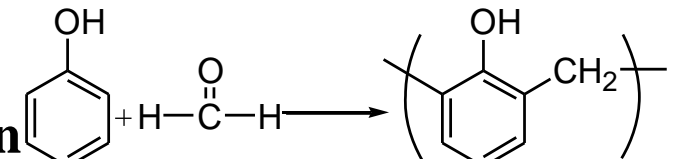
1839 Polystyrene

1860s Poly(ethylene glycol) $\text{+CH}_2\text{CH}_2\text{O+}$

Poly(ethylene succinate) $\text{+OCH}_2\text{CH}_2\text{OC(=O)CH}_2\text{CH}_2\text{C(=O)+}$

early 1900s

Leo Baekeland (Belgian)
Phenol-formaldehyde resin
Bakelite (light-sensitive photographic paper)



The reaction shows a phenol molecule (a benzene ring with an -OH group) reacting with formaldehyde (H-C(=O)-H). The product is a polymer chain segment represented as a benzene ring with an -OH group and a -CH2- group attached to the ring, all enclosed in large parentheses with bonds extending from the parentheses.

1920s Alkyd (polyester) **paints**

Polybutadiene **rubber** $\text{-(CH}_2\text{-CH=CH-CH}_2\text{)-}$

1924 Hermann Staudinger (German)

Introduced the term "Makromolekül"

Proposed that polymers are high MW molecules

Won 1953 Nobel Prize in Chemistry

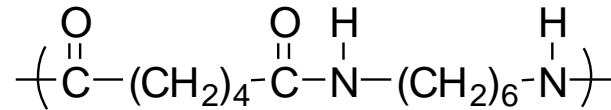
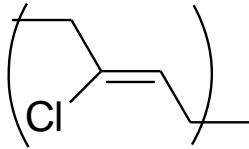
1930s

Wallace Hume Carothers (American)

Proved the theories of Staudinger

Commercialized neoprene rubber

and **polyamide (nylon) fibers**



World War II

Synthetic rubber

1955

Karl **Ziegler** (Germany)

Discovered **coordination polymerization catalyst**

Giulio **Natta** (Italy)

Prepared **stereoregular polymers**

1963

Ziegler and Natta

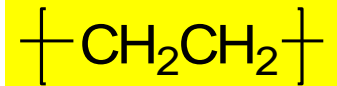
Won **Nobel Prize** in Chemistry

- 1974** Paul **Flory** won **Nobel Prize** in Chemistry
Established **quantitative bases** for polymer behaviors (solution, bulk, crosslinking, chain transfer)
- 1984** Bruce **Merrifield** (**Nobel Prize** in Chemistry)
Invented solid-state **protein** synthesis
- 2000** Alan **MacDiarmid**, Alan **Heeger**, Hideki **Shirakawa** (**Nobel Prize** in Chemistry)
Discovered **conducting polymers** (1977)

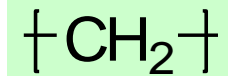
1.2 Definitions



Repeating unit (monomeric unit): Structural unit



Base unit: Smallest possible repeating unit



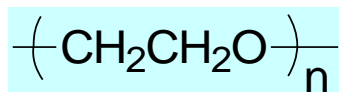
End groups: Structural units that terminate polymer chains

Oligomer: **Oligos (Greek)** → few (when **n** is small)
low molecular weight (MW) polymer

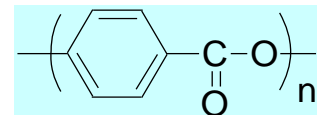
Telechelic polymers: Containing **reactive end groups**
tele (Greek) → far **chele** (Greek) → claw
(e.g., reactive oligomers)

Homochain polymers: Backbones contain pure carbon atom
(polyethylene) $\text{-(CH}_2\text{CH}_2\text{)-}$

Heterochain polymers: Backbones also contain other atoms

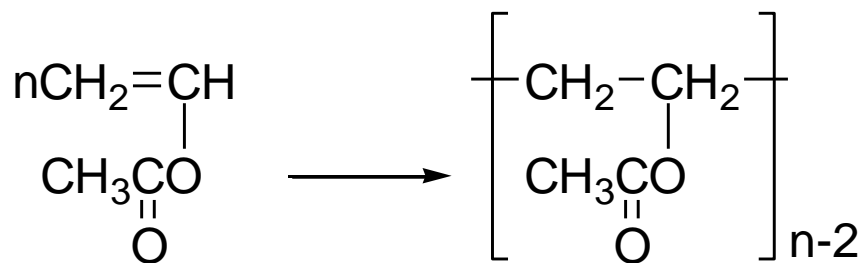


(polyethers, polyesters)



Degree of polymerization (DP): total number of structural units
(including end groups)

Average degree of polymerization: \overline{DP}



(1.5)

$$\mathbf{DP = n - 2 + 2 = n}$$

Classification of polymers

By chemical compositions:

Homopolymer: Contain a single kind of monomer

Copolymers: Contain more than one kind of monomer

(a) **Random** (b) **Alternating** (c) **Block** (d) **Graft**

-A-A-A-A-A-A-A-A-	Homopolymer
-A-B-B-A-B-A-A-B-	Random copolymer
-A-B-A-B-A-B-A-B-	Alternating copolymer
-A-A-A-A-B-B-B-B-	Block copolymer
-A-A-A-A-A-A-A-A- B-B-B-B-B-B-	Graft copolymer



Figure 1.1 Representations of homopolymer and copolymers

diblock: AB **triblock:** ABA; ABC **multiblock:** ABCD...,

By chain structures:

- (a) Linear** (e.g., high density PE)
- (b) Branched** (e.g., low density PE)
- (c) Network** (e.g., cross-linked polymers; elastomers)

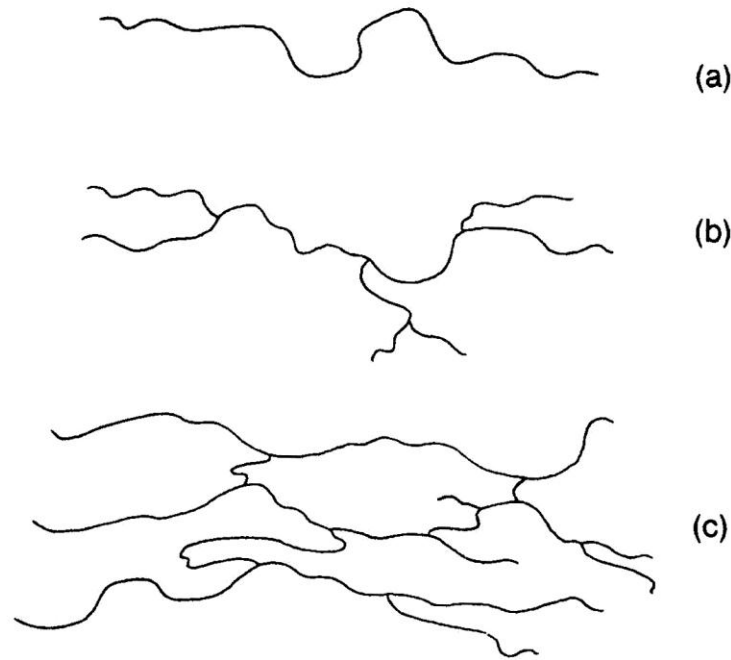


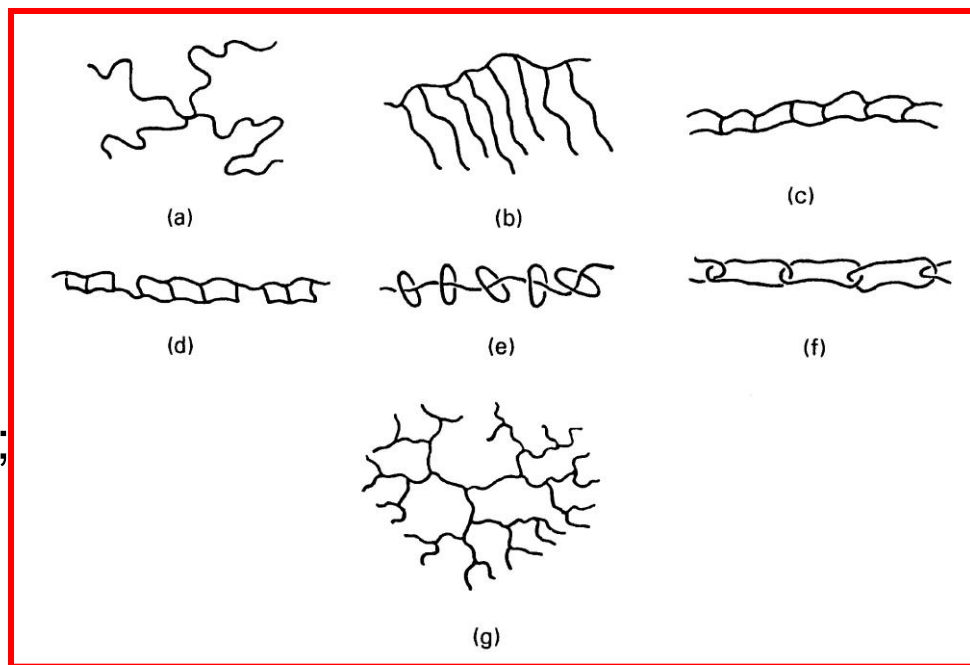
FIGURE 1.2. Representation of polymer types: (a) linear, (b) branched, and (c) network.

By polymer architectures:

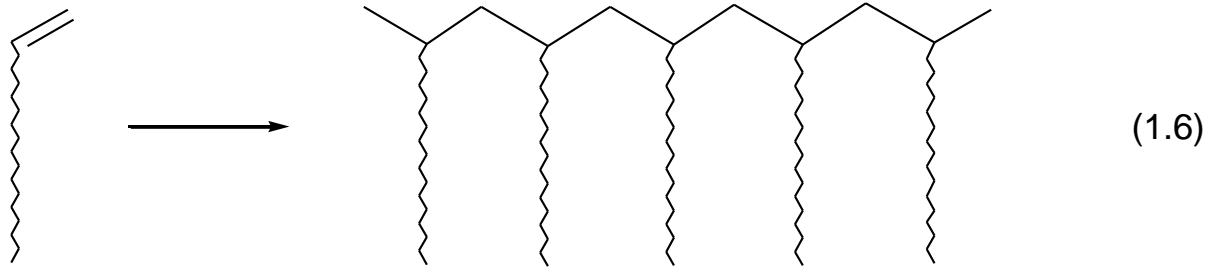
- (a) **Star polymer:** contains ≥ 3 chains emanating from a core
- (b) **Comb polymer:** contains pendant chains
- (c) **Ladder polymer:** has recurring fused-ring structures
- (d) **Semiladder polymer:** has fused-ring sections interspersed with open-chain units
- (e)(f) **Supramolecular assemblies:** molecules linked by noncovalent bonding (polyrotaxane, polycatenane)
- (g) **Dendrimers:** dendritic, starburst, or cascade polymers
dendron (Greek) \rightarrow tree

Figure 1.3 Representations of

- (a) star polymer;
- (b) comb polymer; (c) ladder polymer;
- (d) semiladder(or stepladder) polymer;
- (e) polyrotaxane; (f) polycatenane;
- (g) dendrimer.



Macromonomer (macromer): polymeric or oligomeric monomer



Hyperbranched polymers: extremely branched polymers

Network polymers: polymer chains joined together by covalent bonds will not melt or flow and cannot be molded

- (a) **Vulcanization of rubber (a crosslinking process)**
- (b) **Polymerization of polyfunctional monomers**

Vulcan: the Roman god of fire and metalworking

By processing properties:

Thermosetting polymers: insoluble and only swell
熱固型 (network polymer)

Thermoplastic polymers: not crosslinked, soluble,
熱塑型 will melt and flow
(linear or branched polymer)

By physical or mechanical properties, or end use:

plastics, rubbers (elastomers)
fibers, coatings, adhesives

1.3 Polymerization Process

Polymer classification (traditionally)

Addition polymer: contains the same atoms as the monomer

Condensation polymer: contains fewer atoms than the monomer

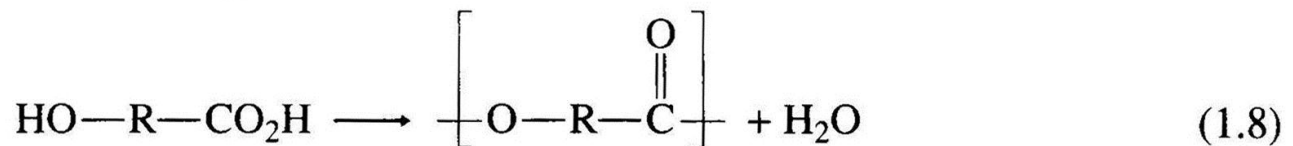
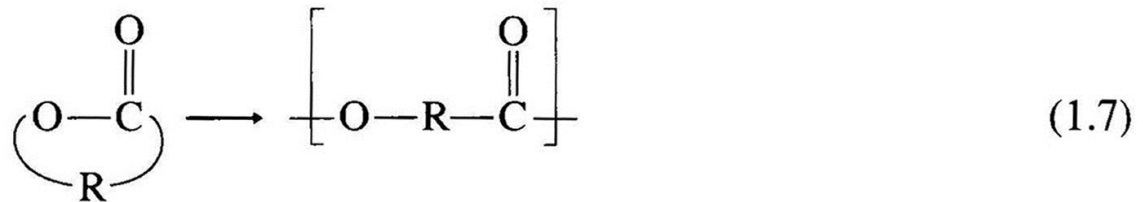
Polymerization process:

Addition, Condensation, Ring opening

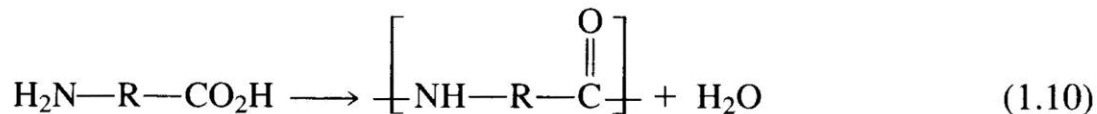
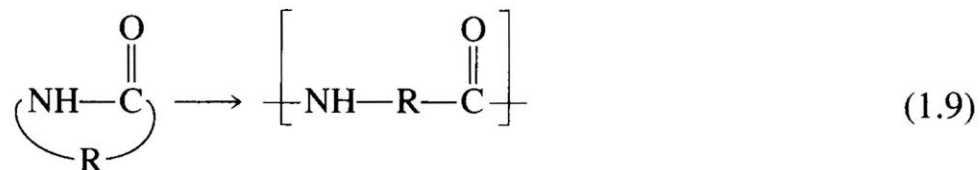
(different processes can produce the same polymer)

Different processes can produce the same polymer

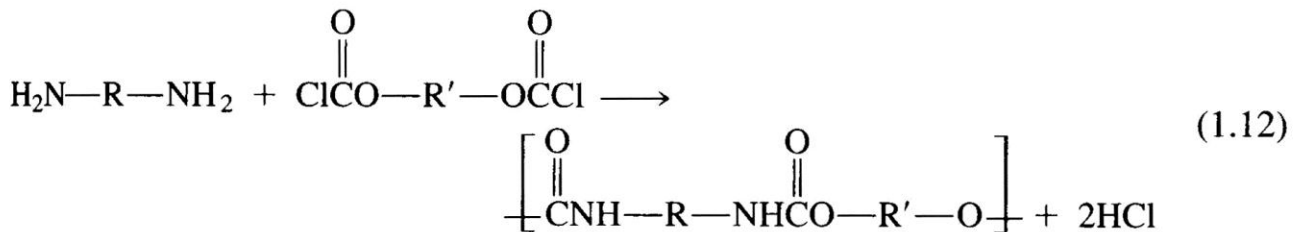
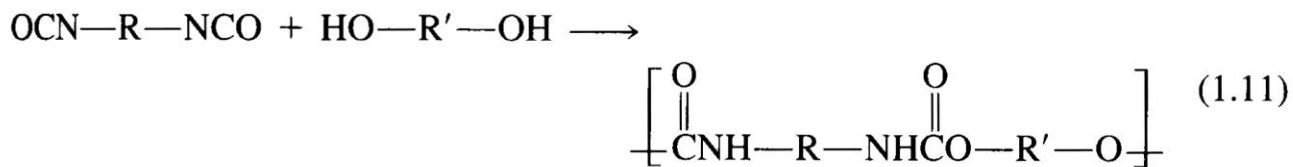
1. Polyester from lactone (1.7), and from ω -hydroxycarboxylic acid (1.8):



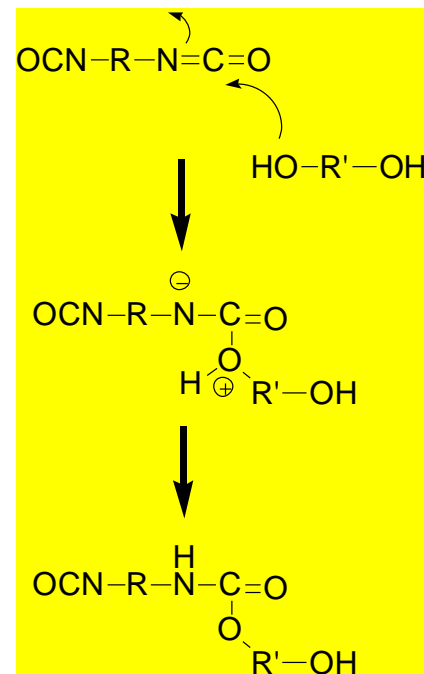
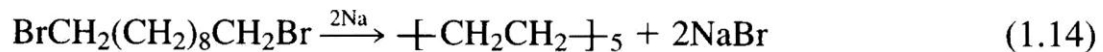
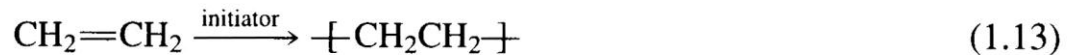
2. Polyamide from lactam (1.9), and from ω -aminocarboxylic acid (1.10):



3. Polyurethane from diisocyanate and dialcohol (1.11), and from diamine and bischloroformate (1.12):



4. Hydrocarbon polymer from ethylene (1.13), and from α,ω -dibromide (1.14):



Classified by polymerization mechanism:

- (1) **step-reaction** or step-growth polymerization
- (2) **chain-reaction** or chain-growth polymerization
- (3) **ring-opening polymerization** (step- or chain-growth)

Polymers prepared via different mechanisms

may have very different properties

(with different MW, end groups, stereochemistry, chain branching)

1.4 Step-reaction Polymerization



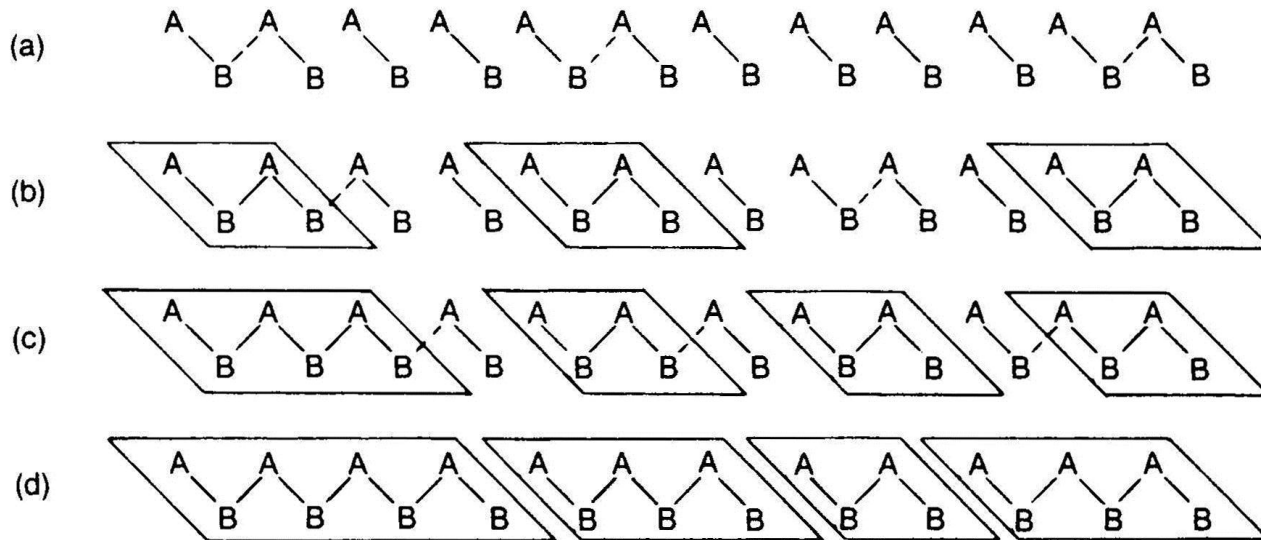


FIGURE 1.4. Step-reaction polymerization: (a) unreacted monomer; (b) 50% reacted, $\overline{DP} = 1.3$; (c) 75% reacted, $\overline{DP} = 1.7$; (d) 100% reacted, $\overline{DP} = 3$. (Broken lines represent reacting species.)

Carothers

p : conversion ratio N_0 : initial number of molecules
 N : the total number of molecules at a given time

$$p = \frac{N_0 - N}{N_0} \quad N = N_0(1-p)$$

$$\overline{DP} = \frac{N_0}{N} = \frac{1}{1-p}$$

$$\text{at 98\% conversion: } \overline{DP} = \frac{1}{1-0.98} = 50$$

\overline{DP} is usually not high

To obtain very high MW polymers:

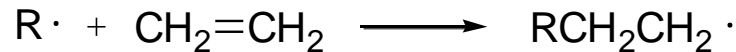
- use very pure monomer
- use an exact stoichiometric ratio

1.5 Chain-reaction Polymerization

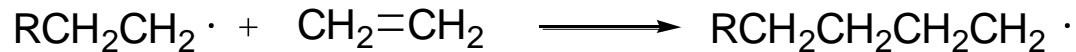
Possible initiators: radical, anion, cation, metal complex

Kinetic steps: initiation, propagation, termination

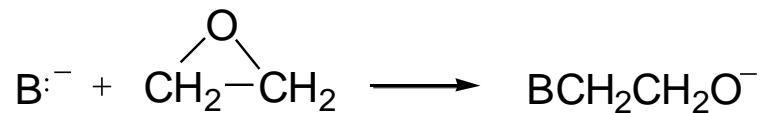
Initiation



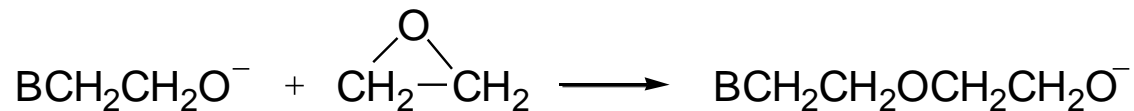
Propagation



Initiation



Propagation



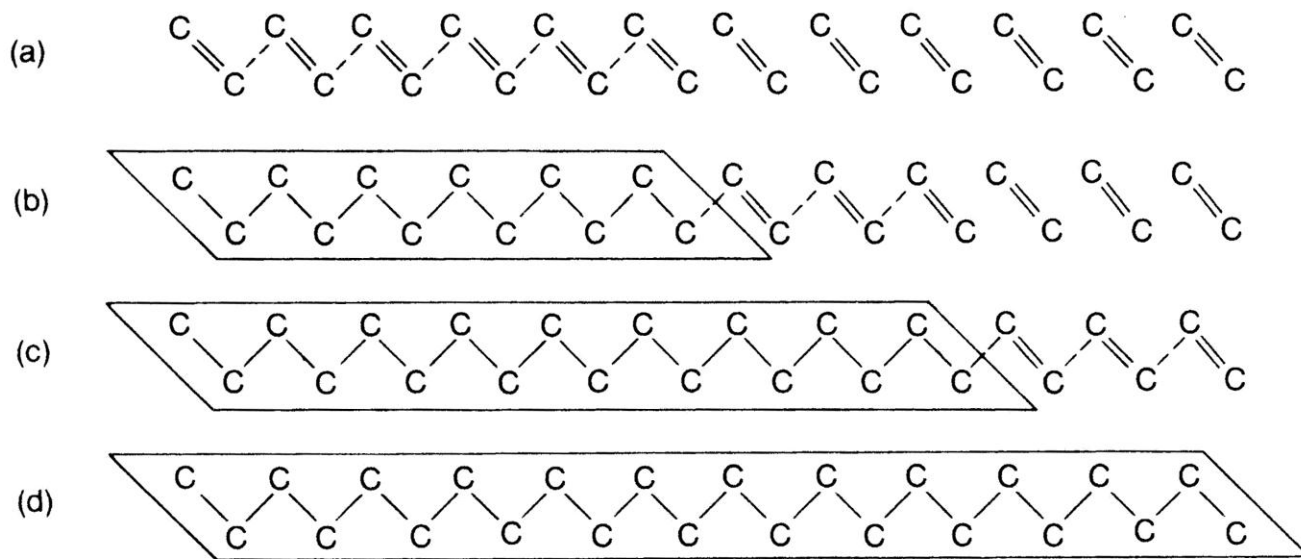


FIGURE 1.5. Chain-reaction polymerization: (a) unreacted monomer; (b) 50% reacted, $\overline{DP} = 1.7$; (c) 75% reacted, $\overline{DP} = 3$; (d) 100% reacted, $\overline{DP} = 12$. (Broken lines represent reacting species.)

Table 1.1. Comparison of Step-Reaction and Chain-Reaction Polymerization

Step Reaction	Chain Reaction
Growth occurs throughout matrix by reaction between monomers, oligomers, and polymers	Growth occurs by successive addition of monomer units to limited number of growing chains
\overline{DP}^a low to moderate	\overline{DP} can be very high
Monomer consumed rapidly while molecular weight increases slowly	Monomer consumed relatively slowly, but molecular weight increases rapidly
No initiator needed ; same reaction mechanism throughout	Initiation and propagation mechanisms different
No termination step ; end groups still reactive	Usually chain-terminating step involved
Polymerization rate decreases steadily as functional groups consumed	Polymerization rate increase initially as initiator units generated; remains relatively constant until monomer depleted

^a \overline{DP} , average degree of polymerization.

1.6 Step-reaction Addition and Chain-reaction Condensation

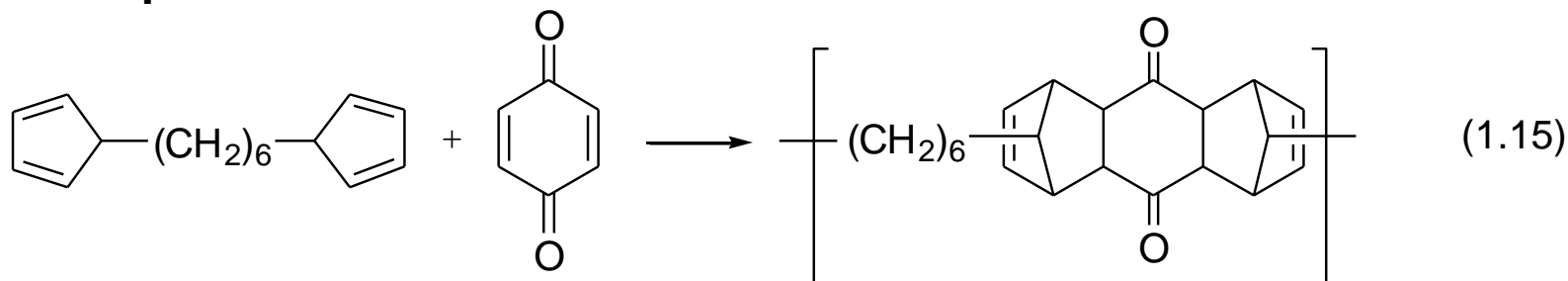
Traditionally —

Step-reaction polymerization \leftrightarrow condensation process

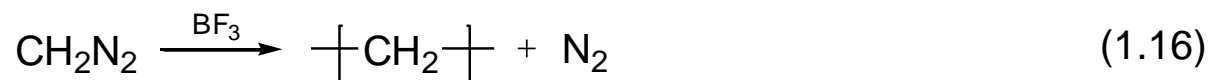
Chain-reaction polymerization \leftrightarrow addition process

New types —

Step-reaction / addition



Chain-reaction / condensation



IUPAC, 1994

Polycondensation — step-reaction, with byproducts

Polyaddition — step-reaction, without byproducts

Chain polymerization — chain-reaction, without byproducts

Condensative chain polymerization — chain-reaction, with byproducts

1.7 Nomenclature

Source-based system — widely accepted

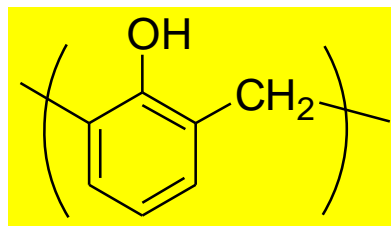
IUPAC system — not widely used

Polymer types (or families) → based on functional groups

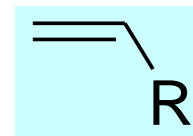
polyesters, polyamides (Nylon), polyethers, polyetherimide

Complicated structure → based on monomers employed

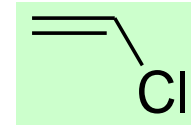
phenol-formaldehyde polymers



Polyolefins — polymers from simple alkenes



Vinyl polymers — polymers from alkenyl monomers
(via chain-reaction polymerization)



Vinyl: vinyl chloride, $\text{CH}_2=\text{CHCl}$

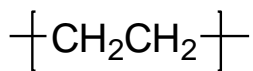
Vinylidene: vinylidene chloride, $\text{CH}_2=\text{CCl}_2$

1.7.1 Vinyl Polymers

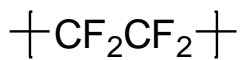
Vinyl polymers — poly(monomer)

based on common name system

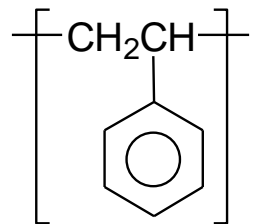
Trade name — **teflon** (du Pont) → polytetrafluoroethylene



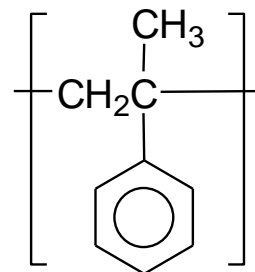
Polyethylene



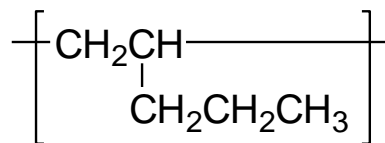
Polytetrafluoroethylene



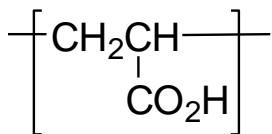
Polystyrene



Poly(α -methylstyrene)



Poly(1-pentene)



Poly(acrylic acid)

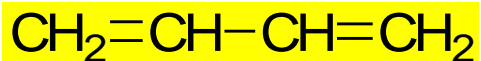
IUPAC — derived from **base unit**,
or **constitutional repeating unit (CRU)**

1. The **smallest structural unit (CRU)** is identified.
2. **Substituent groups** on the backbone are assigned the lowest possible numbers.
3. The name is placed in **parentheses** (or brackets and parentheses, where necessary), and **prefixed with *poly***.

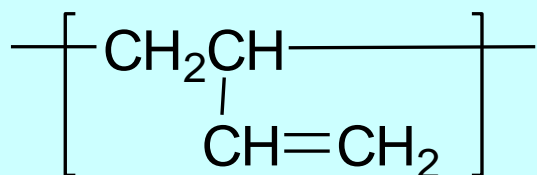
<i>Source name</i>	<i>IUPAC name</i>
Polyethylene	Poly(methylene) $\text{-(CH}_2\text{-CH}_2\text{)-}$
Polytetrafluoroethylene	Poly(difluoromethylene) $\text{-(CF}_2\text{CF}_2\text{)-}$
Polystyrene	Poly(1-phenylethylene) $\text{-(}\underset{\text{Ph}}{\text{CH}}\text{-CH}_2\text{)-}$
Poly(acrylic acid)	Poly(1-carboxylatoethylene) $\text{-(}\underset{\text{COOH}}{\text{CH}}\text{-CH}_2\text{)-}$
Poly(α -methylstyrene)	Poly(1-methyl-1-phenylethylene) $\text{-(}\underset{\text{Ph}}{\overset{\text{Me}}{\text{C}}}\text{-CH}_2\text{)-}$
Poly(1-pentene)	Poly[1-(1-propyl)ethylene] $\text{-(}\underset{\text{Pr}}{\text{CH}}\text{-CH}_2\text{)-}$

IUPAC — parentheses are always used

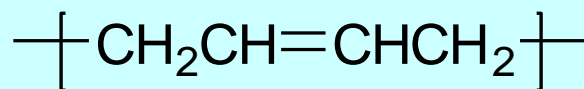
1,3-butadiene



Poly(1,3-butadiene)



1,2-addition



1,4-addition

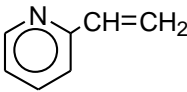
	<i>Source name</i>	<i>IUPAC name</i>
1,2-addition	1,2-Poly(1,3-butadiene)	Poly(1-vinylethylene)
1,4-addition	1,4-Poly(1,3-butadiene)	Poly(1-butene-1,4-diyl)

* **cis/ trans** — in front of the name

Chemical Abstracts/ Polymer Handbook —

adopted the IUPAC name

Table 1.2. Representative Nomenclature of Vinyl Polymers

<i>Monomer Structure</i>	<i>Monomer Name</i>	<i>Polymer Repeating Unit</i>	<i>Source Name</i>	<i>IUPAC^a Name</i>
$\text{CH}_3\text{CH}=\text{CH}_2$	Propylene	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{CH}_3 \end{array} \right]$	Polypropylene	Poly(propylene)
$\text{CH}_2=\text{CHCl}$	Vinyl chloride	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{Cl} \end{array} \right]$	Poly(vinyl chloride)	Poly(1-chloroethylene)
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	Isobutylene	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2\text{CH} \\ \\ \text{CH}_3 \end{array} \right]$	Polyisobutylene	Poly(1,1-dimethylethylene)
$\text{CH}_2=\text{CHCN}$	Acrylonitrile	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{CN} \end{array} \right]$	Polyacrylonitrile	Poly(1-cyanoethylene)
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{CCO}_2\text{CH}_3 \end{array}$	Methyl methacrylate	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2\text{C} \\ \\ \text{CO}_2\text{CH}_3 \end{array} \right]$	Poly(methyl methacrylate)	Poly[1-(methoxycarbonyl)-1-methylethylene]
$\text{CH}_2=\text{CHOC}(=\text{O})\text{CH}_3$	Vinyl acetate	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{OC}(=\text{O})\text{CH}_3 \\ \\ \text{O} \end{array} \right]$	Poly(vinyl acetate)	Poly(1-acetoxyethylene)
	2-Vinylpyridine	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{C}_5\text{H}_4\text{N} \end{array} \right]$	Poly(2-vinylpyridine)	Poly[1-(2-pyridinyl)ethylene]
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \end{array}$	Isoprene	$\left[\begin{array}{c} \text{CH}_2 \quad \text{CH}_2 \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{CH}_3 \quad \text{H} \end{array} \right]$	<i>cis</i> -1,4-Polyisoprene	<i>cis</i>-Poly(1-methyl-1-butene-1,4-diyl)
$\begin{array}{c} \text{Cl} \\ \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \end{array}$	Chloroprene	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{ClC}=\text{CH}_2 \end{array} \right]$	3,4-Polychloroprene	Poly[1-(1-chlorovinyl)ethylene]

^aIUPAC, International Union of Pure and Applied Chemistry.

1.7.2 Vinyl Copolymers

Copolymer: contains more than one species of monomer

Terpolymer: contains three different monomers

Styrene-methyl methacrylate copolymer

IUPAC — recommends source-based name

Poly[styrene-*co*-(methyl methacrylate)]

Copoly(styrene/methyl methacrylate)

Systematic

Poly[styrene-*alt*-(methyl methacrylate)]

Polystyrene-*block*-poly(methyl methacrylate)

Polystyrene-*graft*-poly(methyl methacrylate)

Concise

Alt-copoly(styrene/methyl methacrylate)

Block-copoly(styrene/methyl methacrylate)

Graft-copoly(styrene/methyl methacrylate)

Poly[styrene-*co*-butadiene-*co*-(vinyl acetate)]

Copoly(styrene/butadiene/vinyl acetate)

Polystyrene-*block*-polyisoprene-*block*-polystyrene

Block-copoly(styrene/isoprene/styrene)

Poly[styrene-*alt*-(maleic anhydride)]-*block*-poly(vinyl chloride)

Block-copoly[*alt*-*co*(styrene/maleic anhydride)]-*block*-poly(vinyl chloride)

Polybutadiene-*block*-(polystyrene-*graft*-polyacrylonitrile)

Block-copoly[butadiene/*graft*-*co*(styrene/acrylonitrile)]

1.7.3 Nonvinyl Polymers

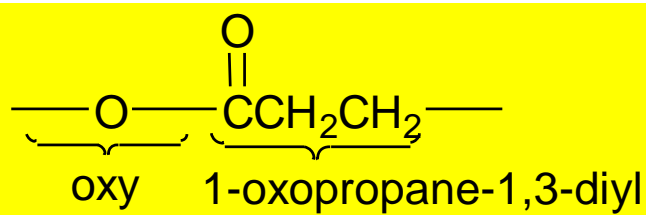
Polyether — According to monomer used (source)
or structure (IUPAC)

Polyester —

For ring opening polymer of cyclic esters (lactones) —

Common: according to the source or the ester repeating unit
poly(β -propiolactone), poly(3-propionate)

IUPAC: based on two subunits of the CRU
poly[oxy(1-oxopropane-1,3-diyl)]

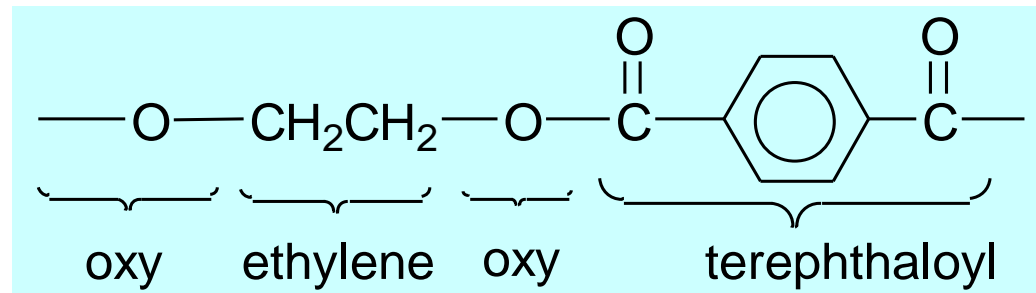


older IUPAC name:
poly[oxy(1-oxotrimethylene)]

PET —

Common: poly(ethylene terephthalate)

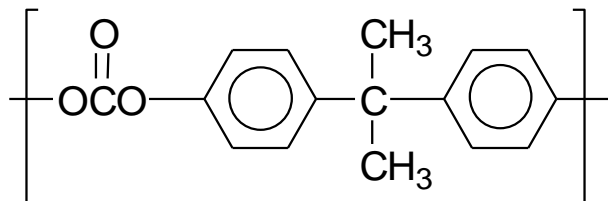
IUPAC: poly(oxyethylene oxyterephthaloyl)



Polycarbonate —

Common: bisphenol A polycarbonate

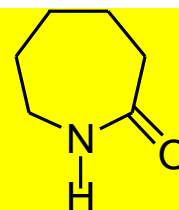
IUPAC: poly(oxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene)



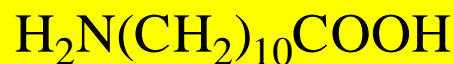
Polyamide — Similar to polyester system

IUPAC: imino **Common:** nylon (for aliphatic polyamides)

from cyclic amides (lactams) — nylon 6



from amino acids — nylon 11

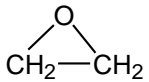

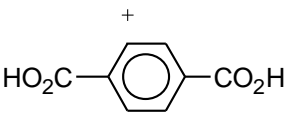


from diamines and dicarboxylic acids — nylon 610 (6-10; 6,10)

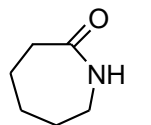
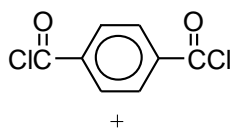
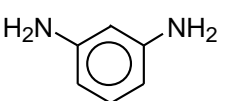
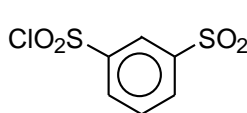


More than one heteroatom — seniority (O > S > N > P)
(e. g. sulfonyl > imino; see **Table 1.3**)

Table 1.3. Representative Nomenclature of Nonvinyl Polymers

<i>Monomer Structure</i>	<i>Monomer Name</i>	<i>Polymer Repeating Unit</i>	<i>Source or Common Name</i>	<i>IUPAC Name</i>
<i>Polyethers</i>				
	Ethylene oxide	$\text{-(CH}_2\text{CH}_2\text{O)-}$	Poly(ethylene oxide)	Poly(oxyethylene)
HOCH ₂ CH ₂ OH	Ethylene glycol	$\text{-(CH}_2\text{CH}_2\text{O)-}$	Poly(ethylene glycol)	Poly(oxyethylene)
CH ₂ O	Formaldehyde	$\text{-(CH}_2\text{O)-}$	Polyformaldehyde	Poly(oxymethylene)
CH ₃ CHO	Acetaldehyde	$\text{-(}\underset{\text{CH}_3}{\text{CHO}}\text{-)}$	Polyacetaldehyde	Poly(oxyethylidene)
<i>Polyesters</i>				
	β -Propiolactone	$\text{-(OCH}_2\text{CH}_2\text{C(=O)-)}$	Poly(β -propiolactone) or poly(3-propionate)	Poly[oxy(1-oxopropane-1,3-diyl)]
HO(CH ₂) ₉ CO ₂ H	10-Hydroxydecanoic acid	$\text{-(O(CH}_2\text{)}_9\text{C(=O)-)}$	Poly(10-decanoate)	Poly[oxy(1-oxodecane-1,10-diyl)]
HOCH ₂ CH ₂ OH + 	Ethylene glycol + Terephthalic acid	$\text{-(OCH}_2\text{CH}_2\text{OC(=O)-C}_6\text{H}_4\text{-C(=O)-)}$	Poly(ethylene terephthalate)	Poly(oxyethylene-oxyterephthaloyl)

Polyamides

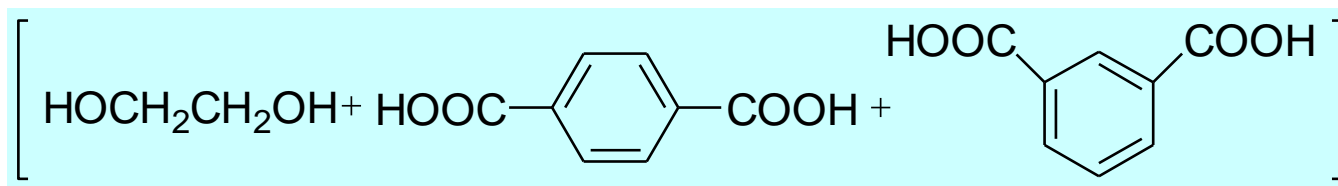
	Caprolactam	$\left[\text{NH}(\text{CH}_2)_5\overset{\text{O}}{\parallel}{\text{C}} \right]$	Polycaprolactam or nylon 6	Poly[imino(1-oxohexane-1,6-diyl)]
$\text{H}_2\text{N}(\text{CH}_2)_{10}\text{CO}_2\text{H}$	11-Aminoundecanoic acid	$\left[\text{NH}(\text{CH}_2)_{10}\overset{\text{O}}{\parallel}{\text{C}} \right]$	Poly(11-undecanoamide) or nylon 11	Poly[imino(1-oxoundecane-1,11-diyl)]
$\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ + $\text{HO}_2\text{C}(\text{CH}_2)_8\text{CO}_2\text{H}$	Hexamethylenediamine + Sebacic acid	$\left[\text{NH}(\text{CH}_2)_6\text{NHC}(\text{CH}_2)_8\overset{\text{O}}{\parallel}{\text{C}} \right]$	Poly(hexamethylene sebacamide) or nylon 610	Poly(iminohexane-1,6-diyliminosebacoyl)
 + 	Terephthaloyl chloride + <i>m</i> -Phenylenediamine	$\left[\text{NH} \text{---} \text{C}_6\text{H}_4 \text{---} \text{NHC}(\text{O}) \text{---} \text{C}_6\text{H}_4 \text{---} \overset{\text{O}}{\parallel}{\text{C}} \right]$	Poly(<i>m</i> -phenylene-terephthalamide)	Poly(imino-1,3-phenylene-iminoterephthaloyl)
$\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2$ + 	Tetramethylenediamine + <i>m</i> -Benzenedisulfonyl chloride	$\left[\text{NH}(\text{CH}_2)_4\text{NHO}_2\text{S} \text{---} \text{C}_6\text{H}_4 \text{---} \text{SO}_2 \right]$	Poly(tetramethylene- <i>m</i> -benzenesulfonamide)	Poly(sulfonyl -1,3-phenylene-sulfonyliminobutane-1,4-diyl imino)

More than one heteroatom — seniority (O > S > N > P)
 (e. g. sulfonyl > imino; see **Table 1.3**)

1.7.4 Nonvinyl Copolymers

IUPAC — Recommends source-based nomenclature

Copolyester from 2:1:1 of ethylene glycol, terephthalic acid and isophthalic acid



Poly(ethylene terephthalate-co-ethylene isophthalate)

Copolyamide from 6-aminohexanoic acid
and 11-aminoundecanoic acid



Poly[(6-aminohexanoic acid)-co-(11-aminoundecanoic acid)]

Poly[(6-hexanoamide)-co-(11-undecanoamide)] (see Table 1.3)

1.7.5 End Groups



1.7.6 Abbreviations (Appendix A)

PVC: Poly(vinyl chloride)

HDPE, LDPE: High- and low-density polyethylene

PET: Poly(ethylene terephthalate)

1.8 Industrial Polymers

Classifications

By mechanical property (modulus; stiffness) —
fibers, plastics, rubbers (elastomers)

By end use — adhesives, coatings

By source — synthetic, natural

Natural polymers — cellulose fibers (cotton, sisal)
protein fibers (wool, silk)
natural rubber

1.8.1 Plastics

Total volume of plastics consumed in 1980s
overtook that of iron and steel

Reasons —

1. weigh less
2. more corrosion resistant
3. less energy consumption

Commodity plastics — high volume, low cost, disposable items
polyethylene, polypropylene, poly(vinyl chloride), polystyrene

HDPE (>0.94 g/cm³) — linear

LDPE (<0.94 g/cm³) — branched

MDPE (0.926-0.940 g/cm³)

Table 1.4. Commodity Plastics

<i>Type</i>	<i>Abbreviation</i>	<i>Major Uses</i>
Low-density polyethylene	LDPE	Packaging film , wire and cable insulation, toys, flexible bottles, housewares, coatings
High-density polyethylene	HDPE	Bottles, drums , pipe, conduit, sheet, film, wire and cable insulation
Polypropylene	PP	Automobile and appliance parts , furniture, cordage, webbing, carpeting, film packaging
Poly(vinyl chloride)	PVC	Construction, rigid pipe, flooring , wire and cable insulation, film and sheet
Polystyrene	PS	Packaging (foam and film), foam insulation , appliances, housewares, toys

Engineering plastics — higher cost, lower volume, **superior mechanical properties**, greater durability

polyamide, polycarbonate, acetal, poly(phenylene oxide), polyester → 99% of the market

Table 1.5. Principal Engineering Plastics

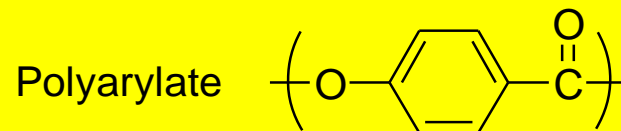
<i>Type</i>	<i>Abbreviation</i>	<i>Chapter Where Discussed</i>
Acetal ^a	POM	11
Polyamide ^b	—	13
Polyamideimide	PAI	13
Polyarylate	—	12
Polybenzimidazole	PBI	17
Polycarbonate	PC	12
Polyester ^c	—	12
Polyetheretherketone	PEEK	11
Polyetherimide	PEI	11
Polyimide	PI	13
Poly(phenylene oxide)	PPO	11
Poly(phenylene sulfide)	PPS	11
Polysulfone ^d	—	11

^aCommon name for polyformaldehyde. Abbreviation refers to poly(oxymethylene).

^bPrincipally nylons 6 and 66.

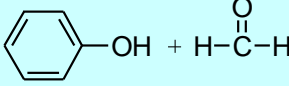
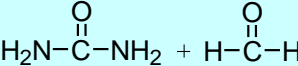
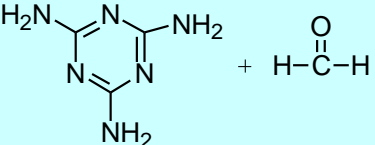
^cPrincipally poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT).

^dSeveral types marketed.



Uses — transportation (automobiles, trucks, aircraft), construction (housing, plumbing, hardware) , electrical goods (business machines, computers), industrial machinery, consumer goods

Table 1.6. Principal Thermosetting Plastics

<i>Type</i>	<i>Abbreviation</i>	<i>Typical Uses</i>	<i>Chapter Where Discussed</i>
Phenol-formaldehyde 	PF	Electrical and electronic equipment, automobile parts, utensil handles, plywood adhesives, particle board binder	14
Urea-formaldehyde 	UF	Similar to PF polymers; also treatment of textiles, coatings	14
Unsaturated polyester	UP	Construction, automobile parts, boat hulls, marine accessories, corrosion-resistant ducting, pipe, tanks, etc., business equipment	12
Epoxy	—	Protective coatings, adhesives, electrical and electronics applications, industrial flooring, highway paving materials, composites	11
Melamine-formaldehyde 	MF	Similar to UF polymers; decorative panels, counter and table tops, dinnerware	14

1.8.2 Fibers

Properties —

high strength and modulus

good elongation (stretchability)

good thermal stability

spinnability

dyeability / chemical resistance / insect and mildew resistance/
crease resistance / luster

Uses: textiles, tire cord, rope, cable

Natural fibers —

cotton (polysaccharide cellulose)

wool, silk (protein)

Synthetic fibers — Cellulosic / Noncellulosic

About 50% of the fiber products

(Nylon + Polyester → 70%)

Table 1.7. Principal Synthetic Fibers

<i>Type</i>	<i>Description</i>
Cellulosic	
Acetate rayon	Cellulose acetate
Viscose rayon	Regenerated cellulose
Noncellulosic	
Polyester	Principally poly(ethylene terephthalate)
Nylon	Includes nylon 66 , nylon 6 , and a variety of other aliphatic and aromatic polyamides
Olefin	Includes polypropylene and copolymers of vinyl chloride , with lesser amounts of acrylonitrile, vinyl acetate, or vinylidene chloride (copolymers consisting of more than 85% vinyl chloride are called <i>vinyon</i> fibers)
Acrylic	Contain at least 80% acrylonitrile ; included are <i>modacrylic fibers</i> comprising acrylonitrile and about 20% vinyl chloride or vinylidene chloride

1.8.3 Rubber (Elastomers)

Exhibit resilience

ability to stretch and retract rapidly

Natural rubber — almost identical to cis-1,4-polyisoprene

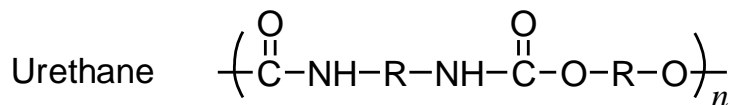
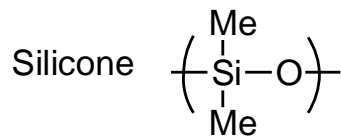
Synthetic rubber — styrene-butadiene, polybutadiene,
(ethylene-propylene (EPDM) → ca. 70%)

Network elastomers — by **crosslinking** between unsaturated
bonds

Non-network elastomers (thermoplastic elastomers) —
block copolymers; **physical crosslinking**

Table 1.8. Synthetic Rubber

<i>Type</i>	<i>Description</i>
Styrene- butadiene	Copolymer; SBR for styrene-butadiene rubber
Poly butadiene	almost entirely <i>cis</i> -1,4 polymer
Ethylene-propylene	EPDM for ethylene-propylene- diene monomer
Poly chloroprene	Principally <i>trans</i> -1,4 polymer; <i>neoprene</i> rubber
Poly isoprene	Mainly <i>cis</i> -1,4 polymer; synthetic natural rubber
Nitrile	Copolymer of acrylonitrile and butadiene (major)
Butyl	Copolymer of isobutylene (major) and isoprene
Silicone	backbone of alternating oxygen and methylated silicon atoms; polysiloxane
Urethane	by linking polyethers through urethane groups



1.8.4 Coatings and Adhesives

Coatings — colored clay (prehistoric artist)

- oils (portraits; landscapes) → eggs (murals) → natural varnishes
- **lacquers** (cellulosenitrate) → **polyester** (alkyd) synthetic varnishes and **paints** (1920s)
- styrene-butadiene copolymer (**interior latex**)
- poly(vinyl acetate), poly(acrylate ester)s (**exterior latex**)

Adhesives — bitumens, natural gums and resins, blood

- **starch**, cellulose nitrate
- **synthetic polymers** (phenol-formaldehyde, urea-formaldehyde polymers)
- **epoxies** and cyanoacrylates

Both require formulations —

solvents, fillers, stabilizers, pigments, other additives

1.9 Polymer Recycling

Making polymers degradable

Incinerating combustible polymers

Recycling (remolding, blending, depolymerization)

Finding innovative uses for used polymers

1988, Society of the Plastic Industry (SPI)

→ Voluntary Plastic Container Coding System

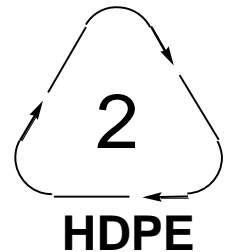


Table 1.9. Plastics Recycling code^a

<i>Number</i>	<i>Letters</i>	<i>Plastic</i>
1	PETE ^b (PET)	Poly(ethylene terephthalate)
2	HDPE	High-density polyethylene
3	V or PVC	Poly(vinyl chloride)
4	LDPE	Low-density polyethylene
5	PP	Polypropylene
6	PS	Polystyrene
7	OTHER	Others or mixed plastics