

Basic Principles of Polymer Chemistry (Part I - Chapter 1 in Stevens)¹

I Polymer Age

A) Classes of Molecules

- 1) Polymer derives from Greek terms “Polymer” = “*poly*” + “*mer*”
 - a) Molecular Weights of thousands to millions
 - b) Many thousands of different molecules even in “pure” samples
 - i) Samples are inhomogeneous
 - ii) Even closely related polymers samples vary by:
 - molecular weights
 - MW distribution
 - degree and type of branching
 - end group identity
 - stereochemistry of side chains
 - etc.
 - iii) Exact structures and structure distributions vary from sample to sample due to differences in:
 - synthetic route
 - exact reaction conditions
 - reagent purity, stoichiometry, etc.
- 2) These properties are fundamentally different from “Discrete” molecules include organics, pharmaceuticals, organometallics, etc., which are typically characterized by:

¹ The graphics in these notes indicated by “Figure/Table/Equation/Etc., x.x in Stevens” are taken from our lecture text: “Polymer Chemistry: An Introduction - 3rd Edition” Malcolm P. Stevens (Oxford University Press, New York,

- a) Molecular Weights typically from a few dozen to a few thousand
 - b) Each molecule in a “pure” sample is identical (except for isotopomers)
 - c) Sample structure independent of preparation route
- 3) Extended Solids
- a) A very large network
 - b) A bulk sample is essentially one molecule with 3-8 bonds between most adjacent atoms
 - c) Most familiar examples to you are solid state materials such as diamond, metal oxides, and minerals

B) Examples of Common Polymers

- 1) polymer synthesis requires difunctional reagents
- 2) “Source” Names are most widely used
 - a) you should know all that we discuss in class, most are pretty self explanatory
 - b) cf. IUPAC names, more later
- 3) Vinyl Polymers are made on largest industrial scale
 - a) ethylene → polyethylene, PE
 - b) vinyl chloride → poly(vinyl chloride), PVC
- 4) Polymers with the same idealized structures can have very different molecular weight distributions and properties when made from different routes
 - a) ethylene oxide → poly(ethylene oxide), PEO
 - b) ethylene glycol → poly(ethylene glycol), PEG

1999).

- 5) All monomers used to prepare a particular polymer can be the same or pairs of matched monomers may be used
- a) ethylene glycol + terephthalic acid \rightarrow poly(ethylene terephthalate). PET
 - b) *para*-hydroxybenzoic acid \rightarrow poly(*para*-hydroxybenzoic acid), PHB

C) Stoichiometry of Polymerizations

- 1) Addition Polymerization
 - a) Mass unchanged (most atom efficient wrt. "Green Chemistry")
 - b) Typically have higher MW and narrower MW distributions
- 2) Condensation Polymerization
 - a) Mass of final polymer lower than mass to monomers
 - b) Small molecules lost (most commonly H₂O, HCl, etc.) during polymerization

D) History of Polymer Chemistry as a Scientific Discipline

- 1) Natural Polymers have been mainstays of human technology since the dawn of time (e.g., leather, string/cloth, paper)
- 2) Term "Polymer" 1st used by Berzelius in 1833
- 3) nitrated cellulose (almost always incorrectly called nitrocellulose)
 - a) Made by HNO₃ derivatization of a natural polymer
 - b) Celluloid (film)
 - c) Gun Cotton
- 4) Styrene polymerization reported 1839 soon after styrene chemistry began but structure was not clear to authors

- 5) poly(ethylene glycol) reported in 1860s with correct structure
- 6) phenol-formaldehyde resin made on commercial scale in early 1900's by Leo Baekeland as "Bakelite" (this is still a very large scale material)
- 7) WWII was a major spur to the polymer industry and supporting science
 - a) Artificial rubber to replace natural Malaysian rubber
 - b) Nylon to replace silk
 - c) Synthetic Fuels \Rightarrow monomeric starting materials
 - d) Invested infrastructure costs

E) Original ideas about Structures

- 1) Were thought to be Colloids (aggregation or association theory) rather than long chains since chains were thought to be unstable
 - a) based on synthetic experience in trying to build longer and longer chains
 - b) based on early Entropy arguments
- 2) Thermodynamic arguments by Hermann Staudinger (Nobel Prize in 1953) and Wallace Carothers
 - a) Quantified when would be stable
 - i) relatively low temperatures
 - ii) $\Delta G = \Delta H - T\Delta S$
 - b) Predicted solution and other properties (i.e., of "Ideal Solutions")
- 3) Polymers were THE "test case" for emerging discipline of Thermodynamics (and also Kinetics) since so many of their properties were at odds with the intuitions of chemists who usually studied discrete molecules

II Definitions of Common Polymer Terms

A) Molecular Size/Weight

1) Monomer \Rightarrow Oligomer \Rightarrow High Oligomer/Low MW Polymer \Rightarrow Polymer

B) Polymer Structure

1) Repeating Unit

a) Conventional Repeating unit depends on monomer used in synthesis, e.g.

i) Polyethylene from Ethylene

ii) Polymethylene from Diazomethane

b) The Base Unit is independent to synthetic route and is smallest possible Repeating Unit

2) End Groups

3) Living Polymers

a) Telechelic Polymers (reactive end groups)

b) Reactive Oligomers

C) Average Degree of Polymerization = DP bar

1) DP = Number of repeating units in chain (plus the number of end groups)

2) DP bar = the Average number of repeating units in sample

3) MW = DP x (Repeating Unit MW)

4) $\text{CH}_3\text{-(CH}_2\text{)}_{100}\text{-CH}_3$ has a DP = 102

D) Types of Atoms in Polymer Backbone**1) Homochain Polymer**

a) e.g., vinyl polymers, polyacetylene, polysulfur, poly(dimethyl silane)

2) Heterochain Polymers

a) e.g., polyesters, polyethers, polyamides

E) Order of repeating units in backbone**1) Figure 1.1 in Stevens****2) Homopolymer (cf. Homochain Polymer)**

a) made from a single monomer (or pair of monomers in cases like polyesters, etc.)

3) Copolymer

a) synthesis

i) made from more than one type of monomer

ii) or occasionally from more than one type of polymer

b) Types of Copolymers

i) Random Copolymer

ii) Block Copolymer

iii) Alternating Copolymer

iv) Graft Copolymer

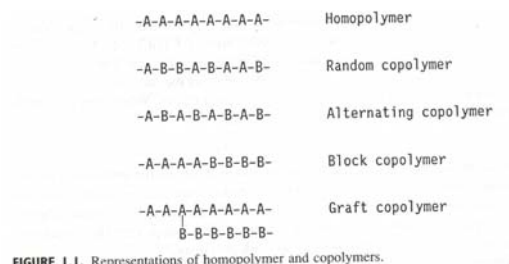
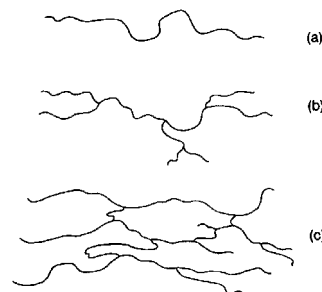
**F) Conventional Polymer Structure Types****1) Figure 1.2 in Stevens****2) Linear**

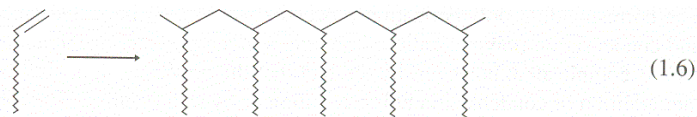
FIGURE 1.2. Representation of polymer types: (a) linear, (b) branched, and (c) network.

a) this is an idealized structure that is very hard to produce in practice

3) Branched

a) may have only a few side chains or may be every few repeating units

b) Equation 1.6 in Stevens



4) Network (Crosslinked)

a) Crosslink density related to “hardness”

b) an average of more than two crosslinks per chain \Rightarrow infinite network

G) Unconventional Polymer Structures

1) Figure 1.3 in Stevens

2) Branched

a) Star

i) has a central core from which 3 or more arms branch

ii) note uses a viscosity modifiers in high performance engine oils

b) Dendrimer (also known as Starburst or Cascade Polymers)

i) generation numbers up to 5-7

ii) near spherical shapes

iii) note steric crowding gradient

iv) note uses for microencapsulation and drug delivery

c) Comb

i) from Macromonomers such as 1-C₂₀H₄₀

ii) very high number of side chains, all of similar length

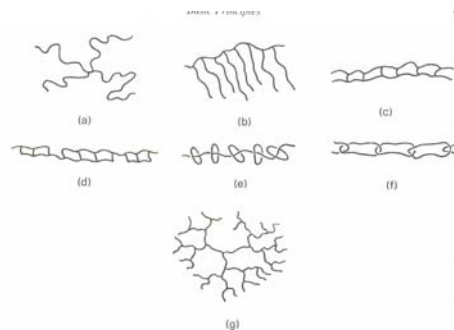


FIGURE 1.3. Representations of (a) star polymer; (b) comb polymer; (c) ladder polymer; (d) semi-ladder (or stepladder) polymer; (e) polyrotaxane; (f) polycatenane; (g) dendrimer.

3) Network**a) Ladder****i) cf. DNA****b) Semiladder (Stepladder)****4) Supramolecular****a) molecular superstructures held together by non-covalent bonds****b) examples****i) Polyrotaxane**

➤ nature of rotaxanes

➤ washers on a wire

ii) Polycatenane

➤ nature of catenanes

➤ chain links

H) Crosslinking**1) Degree of Crosslinking directly correlated with:****a) hardness, elasticity, solvent induced swelling, etc.****b) degree of swelling indicates degree of solvent-polymer compatibility and the degree of crosslinking****2) First “designed” crosslinking process is Vulcanization of rubber (Polyisoprene)****3) Can be via covalent bonds, ionic interactions, or Van der Waals interactions (more later)**

I) Thermoset Polymers

- 1) Example
 - a) phenol-formaldehyde resin (above)
- 2) Properties
 - a) Insoluble
 - b) Non-melting
 - c) Flexibility \Rightarrow Extended Solids
- 3) Thermoset (e.g., Phenol-Formaldehyde) vs. Thermoplastic Polymer (e.g., PE)

J) Classification by Use

- 1) Plastics
- 2) Fibers
- 3) Rubbers (Elastomers)
- 4) Coatings
- 5) Adhesives

III Polymerization Processes

A) Classification of Polymer Reactions at Stoichiometric and Mechanistic Scales

- 1) Reaction Stoichiometric Classification
 - a) Addition vs. Condensation Polymerization
 - b) determined by loss of weight (or not) on polymerization
- 2) Mechanistic Classification
 - a) Step-Growth (Step-Reaction) vs. Chain-Growth (Chain-Reaction)

- b) need intimate reaction details to be certain
- 3) Results of these reaction types (i.e., net stoichiometry vs. reaction mechanism)
 - a) On rate of polymerization
 - b) On MW and MW distribution

B) Examples

- 1) Most (but not all) Step Reaction Polymerizations are also Condensation Reactions
 - a) Chose Examples from those we have had above, e.g.
 - i) polyesters from dicarboxylic acids and diols
 - ii) polyamides from dicarboxylic acids and diamines
 - iii) polyamides from di(acid chlorides) and diamines
 - b) In all of these examples net atoms lost
 - c) In all of these reactions bond formation occurs one step at a time
- 2) Many products can be made by either Chain/Addition or Step/Condensation
 - a) Polyethers from epoxides vs. diols
 - i) Chain/Addition Case: ethylene oxide \rightarrow poly(ethylene oxide), PEO
 - ii) Step/Condensation Case: ethylene glycol \rightarrow poly(ethylene glycol), PEG
 - b) Polyesters from hydroxyacids vs. lactones
 - i) Chain/Addition Case: butyrolactone \rightarrow Poly(butyrolactone)
 - ii) Step/Condensation Case: 4-hydroxybutyric acid \rightarrow Poly(4-hydroxybutyric acid)
 - c) Nylons (Polyamides) from aminocarboxylic acids vs. lactams
 - i) Chain/Addition Case: butyrolactam \rightarrow Poly(butyrolactam)

ii) Step/Condensation Case: 4-aminobutyric acid \rightarrow Poly(4-aminobutyric acid)

3) Some materials can be made by either Step/Addition or Chain/Condensation

a) Polyurethanes from

i) Normal - Step/Condensation Case: diamines + bischloroformates
(ClC(O)O~R~OC(O)Cl) vs.

ii) Bizarre - Step/Addition Case: diisocyanates (OCN~R~NCO) + diols

b) Polyureas from

i) Bizarre - Step/Addition Case: diisocyanates (OCN~R~NCO) + diamines

c) Polyhydrocarbons from

i) Normal - Step/Condensation Case: reduction of alkane dihalides

ii) Normal - Chain/Addition Case: Olefin polymerization

iii) Bizarre - Chain/Condensation: Diazomethane reaction

C) Property Differences Due to Synthetic Route

1) Much more detail later

a) Tremendous variation from batch to batch, lab to lab, route to route

b) Chemical properties generally similar due to similarities in types of “chemical structures”

c) Physical properties markedly different due to differences in “polymer structures”

i) MW & MW distribution

ii) Crosslinking type and density

iii) End group identity

- d) Analytical properties depend on technique with some insensitive and some very sensitive to synthetic route (i.e., IR & EA)

D) Step Reaction Polymerization

- 1) Most commonly found with condensation reactions but there are exceptions
 - a) Bonds formed one at a times
 - b) Most monomer used up quickly but get high MW only near end
 - c) Wide MW distributions typical
- 2) Work out the DP & DP bar for the following
 - a) $DP \approx$ Number of repeating units in chain
 - i) $MW = DP \times (\text{Repeating Unit MW})$
 - b) $DP \text{ bar} =$ **Average** Number of repeating units in chain (plus the number of end groups)
 - i) $MW \text{ bar} = DP \text{ bar} \times (\text{Repeating Unit MW})$
 - ii) $DP \text{ bar} = MW \text{ bar} / \text{Repeating Unit MW} =$ the Average Number of Repeating Units in Chain
 - c) $\rho =$ **Reaction Conversion**
 - i) $\rho = (N_0 - N)/N_0$ where
 - ρ is a measure of which fraction of the original monomers consumed
 - $N_0 =$ number of molecules initially and
 - $N =$ number of molecules finally
 - ii) $DP \text{ bar} = 1 / (1 - \rho)$
 - $\rho = 0$ at start when no polymerization

- $\rho \approx 1$ when polymerization complete (the numerical value of ρ gets closer to 1 at higher final MW)
- for 98% reaction conversion (i.e., $\rho = 0.98$) $\overline{DP} = 50$
- iii) To get high MW you need
 - excellent reaction conversions (i.e., clean reactions that go to completion)
 - very pure reagents (no monofunctional species)
 - very precise reaction stoichiometries

d) **Figure 1.4 in Stevens**

- i) Step Reaction Polymerization of monomer A-B

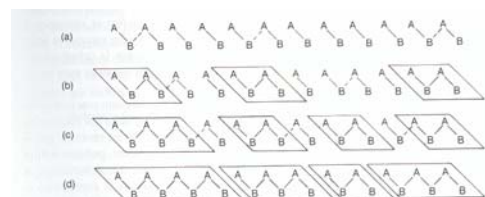


FIGURE 1.4. Step-reaction polymerization: (a) unreacted monomer; (b) 50% reacted, $\overline{DP} = 1.5$; (c) 75% reacted, $\overline{DP} = 1.7$; (d) 100% reacted, $\overline{DP} = 3$. (Broken lines represent reacting species.)

- ii) Show how polymerization effects array of A-B monomers
- iii) Shows how even as ρ approaches 1, the average chain length stays low
- iv) Only at very end when almost no low MW species present do long chains form

E) Chain Reaction Polymerization

- 1) Most commonly found with addition reactions but there are exceptions (e.g., the Chain/Condensation polymerization of diazomethane)
- 2) Generic Mechanisms
 - a) Chain Initiation Step(s)
 - i) generation of highly reactive species, e.g.
 - free radical intermediate
 - carbocation or carbanion

➤ transition metal species

b) Chain Propagation Step(s)

i) 2-3 step which increase MW of growing chain by adding monomers to end of growing chain

c) Chain Termination Step(s)

i) Consume the active species by recombination, etc.

d) Chain Transfer Step(s)

i) May be present and typically modify final polymer structure and MW

3) Commonly found when have highly reactive intermediates

a) Free Radicals, Carbocations, Carbanions, etc.

4) Examples

a) FR Polymerization of Ethylene

b) Nucleophilic Polymerization of Ethylene Oxide (Ring Opening)

5) Figure 1.5 in Stevens

a) Chain Reaction Polymerization of monomer A-B

b) Show how polymerization effects array of A-B monomers

c) Even at low values of ρ (reaction conversion), some high MW chains are present

6) Table 1.1 In Stevens

a) Characteristics of Step and Chain Reactions, side by side comparisons

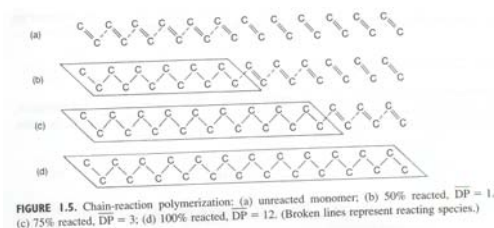


TABLE 1.1. Comparison of Step-Reaction and Chain-Reaction Polymerization

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 increases initially as initiator units generated; remains relatively constant until monomer depleted

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

F) Step-Reaction/Addition & Chain-Reaction/Condensation - Bizarre Reaction Combinations


- 1) Step-Reaction/Addition (described above)
 - a) diisocyanates (OCN~R~NCO) + diols
 - b) diisocyanates (OCN~R~NCO) + diamines
 - c) Diels-Alder reaction of 1,6-bis(cyclopentadienyl)hexanes with benzoquinone
- 2) Chain-Reaction/Condensation (described above)
 - a) Polymerization of CH_2N_2 initiated by BF_3

IV Nomenclature

A) Vinyl Homopolymers), Homochain Polymers

- 1) **Table 1.2 in Stevens**
- 2) Source Names depend on monomer (we will not typically use IUPAC names) for Vinyl Type Polymers
 - a) Ethylene → **Polyethylene, PE**
 - b) (Methylene → Polymethylene)
 - c) Propylene → **Polypropylene, PP**
 - d) 1-Hexene → Poly(1-hexene)
 - e) 1-Pentene → Poly(1-pentene)
 - f) Isobutylene → Polyisobutylene
 - g) Vinyl Chloride → **Poly(vinyl chloride), PVC**
 - h) Vinylidene Dichloride → Poly(vinylidene dichloride)

TABLE 1.2. Representative Nomenclature of Vinyl Polymers

Monomer Structure	Monomer Name	Polymer Repeating Unit	Source Name	IUPAC* Name
$\text{CH}_2\text{CH}=\text{CH}_2$	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	$\left[\begin{array}{c} \text{CH}_2 \\ \\ \text{C} \\ \\ \text{CH}_3 \end{array} \right]$	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)
$\text{CH}_2=\text{C}(\text{CO}_2\text{CH}_3)$	Methyl methacrylate	$\left[\begin{array}{c} \text{CH}_2 \\ \\ \text{C} \\ \\ \text{CO}_2\text{CH}_3 \end{array} \right]$	Poly(methyl methacrylate)	Poly[1-(methoxycarbonyl)-1-methylethylene]
$\text{CH}_2=\text{CHOC}(=\text{O})\text{CH}_3$	Vinyl acetate	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{O} \\ \\ \text{C} \\ \\ \text{O} \\ \\ \text{CH}_3 \end{array} \right]$	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]
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$	Isoprene	$\left[\begin{array}{c} \text{CH}_2 \\ \\ \text{C} \\ \\ \text{CH}_3 \end{array} \right] \left[\begin{array}{c} \text{CH} \\ \\ \text{H} \end{array} \right]$	cis-1,4-Polyisoprene	cis-Poly(1-methyl-1-butene-1,4-diyl)
$\text{CH}_2=\text{C}(\text{Cl})\text{CH}=\text{CH}_2$	Chloroprene	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{Cl} \\ \\ \text{CH}_2 \end{array} \right]$	3,4-Polychloroprene	Poly[1-(1-chlorovinyl)ethylene]

*IUPAC, International Union of Pure and Applied Chemistry.

- i) Polytetrafluoroethylene → Poly(difluoromethylene), Teflon
 - j) Polystyrene → **Poly(styrene), PS**
 - k) α -Methyl Styrene → Poly(α -methylstyrene)
 - l) Vinyl Acetate → Poly(vinyl acetate)
 - i) later hydrolysis \Rightarrow **Poly(vinyl alcohol), PVA**
 - m) Acrylic Acid → Poly(acrylic acid)
 - n) Methyl Methacrylate → **Poly(methyl methacrylate), PMMA**
 - o) Acrylamide → Polyacrylamide
 - p) Butadiene → Polybutadiene
 - q) Isoprene → Polyisoprene (natural rubber is one type)
 - r) Chloroprene (2-chloro-1,3-butadiene) → polychloroprene
- 3) Table of Source and IUPAC Names
- a) Use Poly as a prefix and in the brackets list the monomer structure with numbers indicating the attachment of side chains
- 4) Diene Names
- a) Use cis- and trans- to indicate geometric isomer
 - b) 1,2- and 1,4- to indicate positions of free double bonds derived from olefin polymerization
 - c) Examples
 - i) 1,2-poly(1,3-butadiene)
 - ii) *cis*-1,4-poly(1,3-butadiene)
 - iii) *trans*-1,4-poly(1,3-isoprene) (natural rubber)

B) Copolymer Names (Systematic vs. Concise names)

- 1) Poly[styrene-*co*-ethylene] or Copoly(styrene/ethylene)
- 2) Poly[styrene-*alt*-ethylene] or *Alt*-Copoly(styrene/ethylene)
- 3) Poly[styrene-*block*-ethylene] or *Block*-Copoly(styrene/ethylene)
- 4) Poly[styrene-*graft*-ethylene] or *Block*-Copoly(styrene/ethylene)
 - a) polyethylene grafted onto polystyrene main chain
- 5) Poly[styrene-*co*-ethylene-*co*-propylene] or Copoly(styrene/ethylene/propylene)

V Nonvinyl Polymers

A) Classes, Typically Heterochain Polymers

- 1) Table 1.3 in Stevens
- 2) Polyethers
 - a) Poly(ethylene oxide) & Poly(ethylene glycol)
 - b) Poly(tetrahydrofuran)
 - c) Polyformaldehyde (*para*-formaldehyde)
 - d) Polyacetaldehyde
- 3) Polyesters
 - a) Poly(ethylene terephthalate)
 - b) Poly(*para*-hydroxybenzene)
- 4) Polyamides
 - a) Nylon 6, Nylon 4, Nylon 10
 - i) Poly(10-decanoamide)

TABLE 1.3. Representative Nomenclature of Nonvinyl Polymers

Monomer Structure	Monomer Name	Polymer Repeating Unit	Source or Common Name	IUPAC Name
	Ethylene oxide	$[-CH_2CH_2O-]$	Poly(ethylene oxide)	Polyoxyethylene
	Ethylene glycol	$[-CH_2CH_2O-]$	Poly(ethylene glycol)	Polyoxyethylene
	Formaldehyde	$[-CH_2O-]$	Polyformaldehyde	Polyoxymethylene
	Acetaldehyde	$[-CH_2CH(O)CH_2-]$	Polyacetaldehyde	Polyoxymethylene
	β -Propiolactone	$[-OCH_2CH_2C(=O)-]$	Poly(β -propiolactone)	Polyoxy(1-oxopropane-1,3-diylo)
	10-Hydroxydecanoic acid	$[-O(CH_2)_9C(=O)-]$	Poly(10-decanoate)	Polyoxy(1-oxodecane-1,10-diylo)
	Ethylene glycol	$[-OCH_2CH_2O-]$	Poly(ethylene terephthalate)	Polyoxyethylene terephthalate
	Terephthalic acid	$[-OCH_2CH_2O-C_6H_4-C_6H_4-]$	Poly(ethylene terephthalate)	Polyoxyethylene terephthalate
	Caprolactam	$[-NH(CH_2)_5C(=O)-]$	Polycaprolactam or nylon 6	Poly[amino(1-oxohexane-1,6-diylo)]
	11-Aminoundecanoic acid	$[-NH(CH_2)_9C(=O)-]$	Poly(11-undecanamide) or nylon 11	Poly[amino(1-oxoundecane-1,11-diylo)]
	Hexamethylenediamine	$[-NH(CH_2)_6NH-]$	Poly(hexamethylene sebacamide) or nylon 6,6	Poly[amino(1,6-diaminohexane-1,6-diylo)]
	Sebacic acid	$[-NH(CH_2)_6NH-C(=O)(CH_2)_8C(=O)-]$	Poly(hexamethylene sebacamide)	Poly[amino(1,3-phenyleneisopropylidene)]
	Terephthaloyl chloride	$[-NH(CH_2)_6NH-C(=O)-C_6H_4-C_6H_4-C(=O)-]$	Poly(hexamethylene terephthalamide)	Poly[amino(1,3-phenyleneisopropylidene)]
	<i>m</i> -Phenylenediamine	$[-NH(CH_2)_6NH-C_6H_4-C_6H_4-C(=O)-]$	Poly(hexamethylene <i>m</i> -terephthalamide)	Poly[amino(1,3-phenyleneisopropylidene)]
	1,3-Phenylenediamine	$[-NH(CH_2)_6NH-C_6H_4-C_6H_4-C(=O)-]$	Poly(hexamethylene <i>m</i> -terephthalamide)	Poly[amino(1,3-phenyleneisopropylidene)]
	4,4'-Diaminodiphenyl ether	$[-NH(CH_2)_6NH-C_6H_4-O-C_6H_4-C(=O)-]$	Poly(hexamethylene <i>m</i> -terephthalamide)	Poly[amino(1,3-phenyleneisopropylidene)]

- b) **Nylon 66**, Nylon 610 (the second number refers to the carboxylic acid derived component)
 - i) Poly(hexamethylene sebacamide)
- c) Kevlar and related polyarylamides
 - i) **Poly(*para*-phenylene terephthalamide)**
 - ii) Made from Terephthalic Acid + *para*-Phenylene Diamine
 - iii) Substituting *meta*-groups \Rightarrow great flexibility
- 5) Polyurethanes
 - a) $[-C(O)-NH-R-NH-C(O)-O-R'-O-]_n-$
- 6) Polyureas
 - a) $[-C(O)-NH-R-NH-C(O)-NH-R'-NH-]_n-$
- 7) Polycarbonates
 - a) $[-C(O)-O-R-O-]_n-$

B) Nonvinyl Copolymer

- 1) More Details Later

VI Industrial Polymers

A) Classification Based on Use

- 1) Categorization based more on end use, additives, etc., than on actual repeating unit structure

B) Plastics (Commodity & Engineering)

- 1) Typically, materials properties limited by relatively low intermolecular forces
 - a) primarily Van der Waals, dipole - induced dipole, & dipole-dipole
 - b) ∴ need relatively high MW to get desired strengths, etc.
- 2) Current volumes greater than metals
- 3) Commodity Plastics

a) **Table 1.4 in Stevens**

b) Cost is the major driving force for market

utility, typically cost on the order 20 to 40 cents a pound

- i) In real world applications, typically designed to meet a set of minimum product specifications at the lowest possible cost
 - ii) a profit margin of a few cents
 - iii) primary cost is that for monomer purchase
 - iv) next largest cost is the capital cost for the facilities/equipment
- c) “Big Five”
- i) LDPE, low-density polyethylene
 - ii) HDPE, high-density polyethylene
 - iii) PP, polypropylene
 - iv) PVC, poly(vinyl chloride)
 - v) PS, polystyrene

TABLE 1.5. Principal Engineering Plastics

Type	Abbreviation	Chapter Where Discussed
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(oxyethylene).

^bPrincipally nylons 6 and 66.

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

^dSeveral types marketed.

TABLE 1.4. Commodity Plastics

Type	Abbreviation	Major Uses
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

4) Engineering Plastics

a) **Table 1.5 in Stevens**

- b) lower volume and higher cost/performance materials
- i) In real world applications, typically designed to meet a set of much more demanding product specifications with a much higher acceptable cost
 - ii) substantially larger profit margins
 - iii) primary cost is that for monomer purchase
 - iv) next largest cost is the capital cost for the facilities/equipment which are typically much higher than for commodity plastics
 - In particular, processing costs are often very high
- c) Mostly Heterochain polymers
- i) the Hydrogen-Bonds hold even relatively short chains together very strongly
 - ii) Also, typically most building blocks are quite highly aromatic in character
- d) More recently some new grades of PE, etc.
- e) Thermosetting Plastics

- i) **Table 1.6 in Stevens**

TABLE 1.6. Principal Thermosetting Plastics

Type	Abbreviation	Typical Uses	Chapter Where Discussed
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

C) Fibers

- 1) **Table 1.7 in Stevens**
- 2) Synthetic and Natural

TABLE 1.7. Principal Synthetic Fibers

Type	Description
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>vinylon</i> fibers)
Acrylic	Contain at least 80% acrylonitrile; included are <i>modacrylic</i> fibers comprising acrylonitrile and about 20% vinyl chloride or vinylidene chloride

D) Rubber (Elastomers)

- 1) Table 1.8 in Stevens
- 2) Synthetic and Natural

TABLE 1.8. Principal Types of Synthetic Rubber

Type	Description
Styrene-butadiene	Copolymer of the two monomers in various proportions depending on properties desired; called SBR for styrene-butadiene rubber
Polybutadiene	Consists almost entirely of the <i>cis</i> -1,4 polymer
Ethylene-propylene	Often abbreviated EPDM for ethylene-propylene-diene monomer; made up principally of ethylene and propylene units with small amounts of a diene to provide unsaturation
Polychloroprene	Principally the <i>trans</i> -1,4 polymer, but also some <i>cis</i> -1,4 and 1,2 polymer; also known as <i>neoprene</i> rubber
Polyisoprene	Mainly the <i>cis</i> -1,4 polymer; sometimes called "synthetic natural rubber"
Nitrile	Copolymer of acrylonitrile and butadiene, mainly the latter
Butyl	Copolymer of isobutylene and isoprene, with only small amounts of the latter
Silicone	Contains inorganic backbone of alternating oxygen and methylated silicon atoms; also called polysiloxane (Chap. 15)
Urethane	Elastomers prepared by linking polyethers through urethane groups (Chap. 13)

E) Coatings

- 1) Would paint by any other name be as sweet
- 2) Efforts to reduce VOC (volatile organic carbon)

F) Adhesives

- 1) Would glue by any other name be as sticky
- 2) Efforts to reduce VOC (volatile organic carbon)

VII Recycling

- A) Table 1.9 in Stevens
- B) Costs of collection and separation
- C) Pre- and Post-consumer recycling
- D) Degradation upon use cycle
- E) Depolymerization \Rightarrow Purification \Rightarrow Repolymerization
- F) Biodegradable, Photodegradable, etc.

TABLE 1.9. Plastics Recycling Code^a

Number	Letters	Plastic
1	PETE ^b	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

^aAdopted by the Society of the Plastics Industry (SPI).^bPET is the more widely accepted abbreviation.