Nomenclature of Polymers:

Polymer nomenclature has been largely a matter of custom without any one system being universally adopted. Though a systematic IUPAC nomenclature now exists for polymers, this nomenclature is rarely used because a common naming system is widely accepted through the force of usage. The common naming system, based either on the source of the polymer, the structure of the polymer, or trade names, usually works without difficulty because the number of polymers that are of interest to the average worker in the field does not exceed a few dozen, and so are not difficult to remember. However, as new polymers enter the area of common usage the number may become too large eventually, necessitating a wider usage of the IUPAC nomenclature.

For the common nomenclature the usual practice is to name a polymer according to its source, i.e., the monomer(s) used in its synthesis, and the generic term used is poly“monomer”, whether or not the monomer is real. The prefix ‘poly’ is added on to the name of the monomer to form a single word, e.g., polyethylene, polystyrene, and polyacrylonitrile. However, when the monomer has a multi-worded name, the name of the monomer after the prefix ‘poly’ is enclosed in parentheses, e.g., poly(vinyl chloride), poly(vinyl alcohol) and poly(methyl methacrylate).

A few polymers are given names based on the repeating unit without reference to the parent monomer. The primary examples are silicones, which possess the repeating unit:

Thus, if $R = \text{CH}_3$, the polymer is named as poly(dimethyl siloxane).

The nomenclature of random copolymers includes the names of the monomers separated by the interfix -co-. Thus the following is named as poly(styrene-co-methyl methacrylate) or poly(methyl methacrylate-co-styrene), the major component being named first.

For alternating copolymers, the interfix -alt- is used, e.g., poly (styrene-alt-maleic anhydride):

Graft copolymers of A and B monomers are named poly(A-g-B) or poly A-graft-poly B with the backbone polymer -(A-)$_n$- mentioned before the branch polymer. Some examples are poly(ethylene-g-styrene) or polyethylene-graft-polystyrene and starch-graft-poly(methylmethacrylate).

In the nomenclature of block copolymers, $b$ or block is used in place of g or graft, e.g., poly(A-b-B) or poly A-block-poly B, poly(A-b-B-b-A) or poly A-block-poly B-block-poly A, poly(A-b-B-b-C) or poly A-block-poly B-block-poly C, and so on. Thus the following triblock polymer is called
poly(styrene-\textit{b}-butadiene-\textit{b}-styrene) or polystyrene-\textit{block}-polybutadiene-\textit{block}-polystyrene. For commercial products, such polymers are usually designated by the monomer initials; thus, this structure is named SBS block copolymer:

Condensation polymers are frequently named from the internal linking group between hydrocarbon portions. Thus, the following, poly(ethylene terephthalate), is a polyester which can be written as -(O-R-O-CO-R-CO)\textsubscript{n}-

and poly(\textit{p}-phenylene terephthalamide) is a polyamide written as -(HN-R-NH-CO-R-CO)\textsubscript{n}-. 

Similarly, -(O-R-O-CO-NH-R'-NH-CO)- is a polyurethane, and -(R-SO\textsubscript{2})\textsubscript{n}- is a polysulfone. The following table is illustrative:

<table>
<thead>
<tr>
<th>Family name</th>
<th>Linkage</th>
<th>Family name</th>
<th>Linkage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamide</td>
<td>\begin{array}{c} \text{H} \ N \end{array}</td>
<td>Polyvinyl</td>
<td>\begin{array}{c} \text{C} \ \text{C} \end{array}</td>
</tr>
<tr>
<td>Polyester</td>
<td>\begin{array}{c} \text{O} \ \text{O} \end{array}</td>
<td>Polyanhydride</td>
<td>\begin{array}{c} \text{C} \ \text{O} \ \text{O} \end{array}</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>\begin{array}{c} \text{O} \ \text{N} \end{array}</td>
<td>Polyurea</td>
<td>\begin{array}{c} \text{N} \ \text{N} \end{array}</td>
</tr>
<tr>
<td>Polyether</td>
<td>\begin{array}{c} \text{O} \end{array}</td>
<td>Polycarbonate</td>
<td>\begin{array}{c} \text{O} \ \text{O} \end{array}</td>
</tr>
<tr>
<td>Polysiloxane</td>
<td>\begin{array}{c} \text{O} \ \text{Si} \end{array}</td>
<td>Polyphosphate ester</td>
<td>\begin{array}{c} \text{O} \ \text{O} \ \text{P} \ \text{O} \end{array}</td>
</tr>
<tr>
<td>Polysulfide</td>
<td>\begin{array}{c} \text{S} \ \text{S} \end{array}</td>
<td>Polysulfone</td>
<td>\begin{array}{c} \text{S} \ \text{S} \end{array}</td>
</tr>
</tbody>
</table>

These commonly used names convey relatively little information about the repeating unit structure.
In the common naming system, condensation polymers are named by analogy with the lower molecular-weight products produced by condensation. Thus, since all esters are named by adding the suffix ‘ate’ to the name of the parent acid (e.g., ethyl acetate), the following polymer is named poly(ethylene terephthalate) according to the parent acid, terephthalic acid, which is a para diacid. The word ‘ethylene’ here implies ‘ethylene glycol’ because the alcohol used must be a glycol if the polymer is to be linear.

Similar reasoning is also followed in naming polyamides. Thus, the word ‘hexamethylene’ in poly(hexamethylene adipamide) obviously implies hexamethylene diamine because the polymeric structure could be made by the condensation reaction of hexamethylene diamine $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$, and adipic acid, HOOC(\text{CH}$_2$)$_4$COOH.

An alternative naming system is often used for synthetic polyamides derived from unsubstituted nonbranched aliphatic monomers. Thus, a polyamide made from either an amino acid or a lactam is called nylon-x, where x is the number of carbon atoms in the repeating unit. A nylon made from a diamine and a dibasic acid is designated by two numbers, the first representing the number of carbons in the diamine chain and the second the number of carbons in the dibasic acid.

**IUPAC Structure-based Nomenclature system**

The basis of IUPAC polymer nomenclature system is the selection of a preferred *constitutional repeating unit* (abbreviated as CRU). The CRU is also referred to as the *structural repeating unit*. The CRU is the smallest possible repeating unit of the polymer. It is a bivalent unit for a single-strand polymer. The name of the polymer is the name of the CRU in parentheses or brackets prefixed by poly. The CRU is synonymous with the repeating unit defined in previous sections except when the repeating unit consists of two symmetric halves, as in the polymers -(CH$_2$CH$_2$)$_n$- and -(CF$_2$CF$_2$)$_n$-. The CRU is CH$_2$ and CF$_2$, respectively, for polyethylene and polytetrafluoroethylene, while the repeating unit is CH$_2$CH$_2$ and CF$_2$CF$_2$, respectively. The constitutional repeating unit is named as much as possible
according to the IUPAC nomenclature rules for small organic compounds. The IUPAC rules for naming single-strand polymers dictate the choice of a single CRU so as to yield a unique name, by specifying both the seniority among the atoms or subunits making up the CRU and the direction to proceed along the polymer chain to the end of the CRU. A CRU is composed of two or more subunits when it cannot be named as a single unit. The following is a summary of the most important of the IUPAC rules for naming single-stand organic polymers:

1. The name of a polymer is the prefix poly followed in parentheses or brackets by the name of the CRU. The CRU is named by naming its subunits. Subunits are defined as the largest subunits that can be named by the IUPAC rules for small organic compounds.

2. The CRU is written from left to right beginning with the subunit of highest seniority and proceeding in the direction involving the shortest route to the subunit next in seniority.

3. The seniority of different types of subunits is heterocyclic rings > heteroatoms or acyclic subunits containing heteroatoms > carbocyclic rings > acyclic subunits containing only carbon. The presence of various types of atoms, groups of atoms, or rings that are not part of the main polymer chain but are substituents on the CRU do not affect this order of seniority.

4. For heterocyclic rings the seniority is a ring system having nitrogen in the ring > a ring system having a heteroatom other than nitrogen in the order of seniority defined by rule 5 below > a ring system having the greatest number of heteroatoms > a ring system having the largest individual ring > a ring system having the greatest variety of heteroatoms > a ring system having the greatest number of heteroatoms highest in the order given in rule 5.

5. For heteroatom(s) or acyclic subunits containing heteroatom(s), the order of decreasing priority is O, S, Se, Te, N, P, As, Sb, Bi, Si, Ge, Sn, Pb, B, H (Any heteroatom has higher seniority than carbon - rule 3.) The seniority of other heteroatoms within this order is determined from their positions in the periodic table.

6. For carbocyclic rings the seniority is a ring system having the greatest number of rings > the ring system having the largest individual ring > the ring system having the greatest number of atoms common to its rings.

7. For a given carbocyclic or heterocyclic ring system: (a) when rings differ only in degree of unsaturation, seniority increases with degree of unsaturation; (b) for the same ring system, seniority is higher for the ring system having the lowest location number (referred to as locant), which designates the first point of difference for ring junctions.

8. These orders of seniority are superseded by the requirement of minimizing the number of free valences in the CRU, that is, the CRU should be a bivalent unit wherever possible.

9. Where there is a choice, subunits should be oriented so that the lowest locant results for substituents.

Let us illustrate some of these rules by naming a few polymers. For the polymer:

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    O    O    O    O    O    O
    F    F    F    F    F    F
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The possible CRUs:
Note that CRUs D-F are simply the reverse of CRUs A-C. Application of the nomenclature rules dictates the choice of only one of these as the CRU. That oxygen has higher seniority than carbon (rule 5) eliminates all except C and D as the CRU. Application of rule 8 results in C as the CRU and the name poly[oxy(1-fluoroethylene)]. Choosing D as the CRU would result in the name poly[oxy(2-fluoroethylene)], which gives the higher locant for the fluorine substituent. The name poly[oxy(fluoromethylene)methylene)] is incorrect because it does not define the largest possible subunit (which is CHFCH₂ vs. CHF plus CH₂).

Rule 7 specifies –CH=CH– as the correct CRU in preference to –CH₂CH₂–, since the former is bivalent, while the latter is tetravalent. The polymer –(CH=CH)ₙ– is poly(ethylene-1,2-diyl).

The higher seniority of heterocyclic rings over carbocyclic rings (rule 3) and the higher seniority with higher unsaturation for cyclic subunits (rule 7a) yield the CRU XV with the name poly(pyridine-2,4-diyl-1,4-phenylene)cyclohexane-1,4-diyl).

The higher seniority of cyclic subunits over acyclic subunits (rule 3) and the higher seniority of a subunit with lower locant(s) relative to the same subunit with higher locant(s) (rule 7b) yield the CRU XVI with the name poly(cyclohexane-1,3-diyl)cyclohexane-1,4-diyl-1-methylpropane-1,3-diyl). Note that all acyclic subunits except CH₂ and CH₂CH₂ are named as alkane-α, ω-diyl. CH₂ and CH₂CH₂ subunits are named methylene and ethylene, respectively.

In the IUPAC system locants are placed immediately before the part of the name to which they apply; for instance, subunits such as pyridine-2,4-diyl and 1-methylpropane-1,3-diyl. One of the few exceptions is the phenylene subunit, for example, 1,4-phenylene in the example previously discussed.

The IUPAC nomenclature system recognizes that most of the common (commercial) polymers have source-based or semisystematic names that are well established by usage. IUPAC does not intend that such names be supplanted by the IUPAC names but anticipates that such names will be kept to a minimum. The IUPAC system is generally used for all except the common polymers. The IUPAC
names for various of the common polymers are indicated below the more established source or semi-systematic name in the following:

\[
\begin{align*}
\text{CH}_2\text{CH}_2 \quad & \text{Polyethylene or polyethene} \\
\text{CH}_2\text{CH}_3 \quad & \text{Polymethylene} \\
\text{CH}_2\text{CH}_2 \quad & \text{Polypropylene or polypropene} \\
\text{CH}_2\text{CH}_3 & \text{Poly(1-methylethylene)} \\
\text{CH}_2\text{CH}_2 \quad & \text{Polystyrene} \\
\text{CH}_2\text{CH}_3 & \text{Poly(1-phenylethylene)} \\
\text{CH}_2\text{CH}_2 \quad & \text{Poly(methyl acrylate)} \\
\text{COOCH}_3 & \text{Poly[1-(methoxycarbonyl)ethylene]} \\
\text{OCH}_2 \quad & \text{Polyformaldehyde} \\
\text{O} & \text{Poly(oxymethylene)} \\
\text{O} & \text{Poly(phenylene oxide)} \\
\text{O} & \text{Poly(oxy-1,4-phenylene)} \\
\text{NH(CH}_2\text{NHC}(\text{CH}_2\text{CO}) \quad & \text{Poly(hexamethylene adipamide)} \\
\text{NHCO(CH}_2\text{NHCO(CH}_2\text{CO}) \quad & \text{Poly(iminohexanediyliminohexane-1,6-diyl)} \\
\text{NHCO(CH}_2\text{NHCO(CH}_2\text{CO}) \quad & \text{Poly(\epsilon-caprolactam) or poly(\epsilon-aminocaproic acid)} \\
\text{OCH}_2\text{CH}_2\text{CO} \quad & \text{depending on the source of polymer} \\
\text{OCH}_2\text{CH}_2\text{CO} \quad & \text{Poly(imino(1-oxohexane-1,6-diyl))]}
\end{align*}
\]
Problems:

1. Name the polyamides made from the following monomers and draw their structural formulas (one repeating unit).

(a) Caprolactam; (b) ω-aminoundecanoic acid; (c) dodecyl lactam; (d) hexamethylene diamine and sebacic acid, and (e) hexamethylene diamine and decanedioic acid.

Ans.

(a) Nylon-6:

(b) Nylon-11:

(c) Nylon-12:

(d) Nylon-6,10:

(d) Nylon-6,10:

2. Represent, by showing a repeating unit, the structure of the polymer which would be obtained by polymerization of the following monomers: (a) ω-aminolauric acid; (b) lauryl lactam; (c) ethylene oxide; (d) oxacyclobutan; (e) ethylene glycol and terephthalic acid; (f) hexamethylene diamine and sebacic acid; (g) ethylene glycol and m-phenylene diisocyanate; (h) m-phenylene diamine and isophthaloyl chloride.

(a) from H₂N

12-aminododecanoic acid

(b) from

laurolactam

c) from

(d) from
3. Draw the structural formula (one repeating unit) for each of the following polymers: (a) poly(4-methylpent-1-ene); (b) poly(chlorotrifluoroethylene); (c) poly(vinyl ethyl ether); (d) poly(vinylidene chloride); (e) polyethylenimine; (f) poly(methyl-2-cyano-acrylate); (g) polychloroprene; (h) poly(butylene terephthalate); (i) poly(1,2-propylene oxalate); (j) poly(diisoxymethylcyclohexyl terephthalate); (k) poly-caprolactam (nylon-6); (l) polyformaldehyde; (m) poly-oxymethylene; (n) poly(propylene oxide); (o) poly (propylene glycol); (p) poly(4-phenylene sulfone); (q) poly(dimethyl siloxane); (r) poly (vinyl butyral); (s) poly (p-phenylene); (t) poly(p-xylylene); (u) polycaprolactone.