

I. Introduction to Polymer Concepts

A. Types of Polymers and Polymerization

The following fundamental concepts and definitions are critical to a proper understanding of topics to be later discussed:

Polymer - Large molecule built up by the linking together of large numbers of smaller molecules.

Monomers - Small molecules, which are linked together to form polymer molecules.

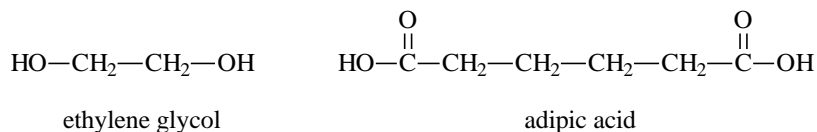
Polymerization - The chemical reaction by which monomers are linked to form polymers. Two basic types of polymerization are recognized:

1. Step growth (mechanistic classification)
Condensation (structural classification)
2. Chain growth (mechanistic classification)
Addition (structural classification)

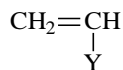
Structural unit - The residue of each type of monomer unit incorporated into a polymer.

Repeating unit - The smallest grouping of atoms, which defines the structure of a polymer. This unit is generally connected end-to-end and repeats many times to form the polymer chain.

Difunctional monomer - The most common type of monomer used in step-growth polymerizations. Examples are ethylene glycol, a diol, and adipic acid, a dicarboxylic acid.



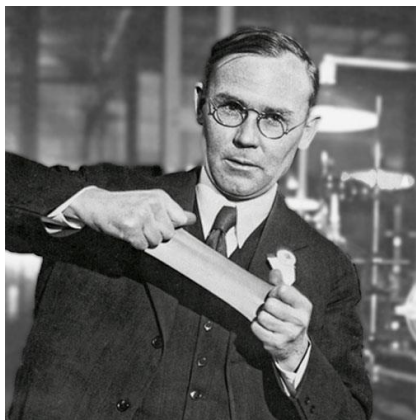
Vinyl monomer - The most common type of monomer used in chain-growth polymerization. The general structure of a vinyl monomer is,



where, Y may be almost any functional group.

1. Polymer Composition and Structure

Wallace Carothers, the inventor of nylon, and arguably the most important figure in the early development of step-growth polymerization, originally classified polymers as either condensation and addition polymers, on the basis of the compositional difference between the polymer and the monomer(s) from which it was synthesized.

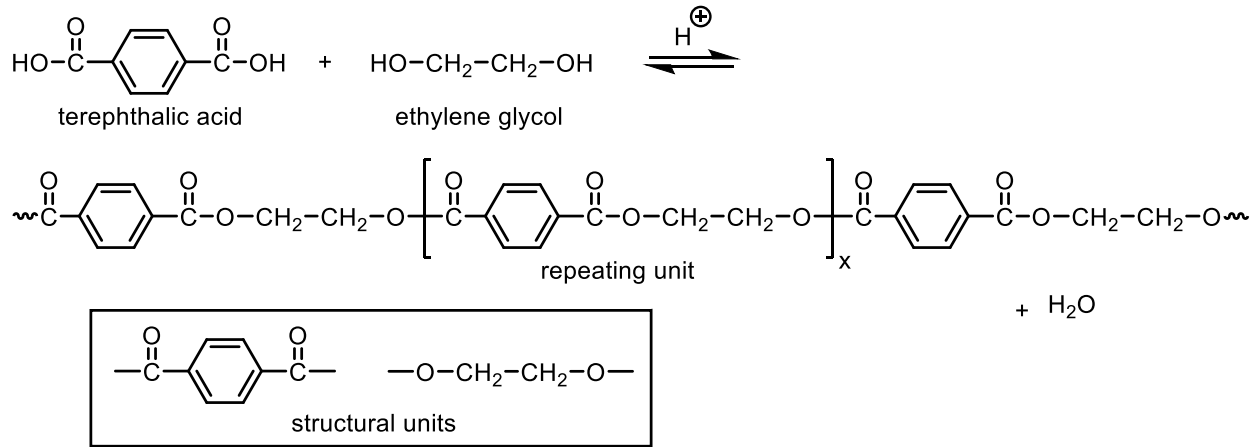


Wallace Carothers

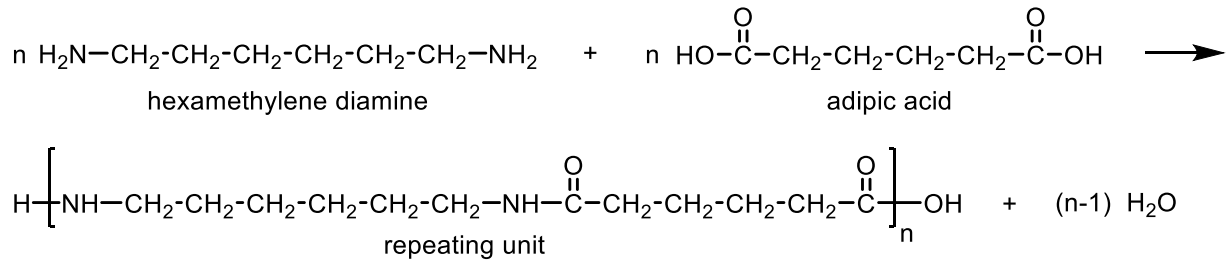
According to Carothers, condensation polymers were those that were formed from polyfunctional monomers by the various condensation reactions of organic chemistry, usually (but not always) with the elimination of a small molecule such as water or HCl. These reactions created polymers with characteristic chemical linkages along the chain. Examples include:

<u>Polymer Type</u>	<u>Characteristic Chemical Linkage</u>
Polyester	$\begin{array}{c} \text{O} \\ \\ \text{---C---O---} \end{array}$
Polyamide	$\begin{array}{c} \text{O} \\ \\ \text{---C---NH---} \end{array}$
Polycarbonate	$\begin{array}{c} \text{O} \\ \\ \text{---O---C---O---} \end{array}$

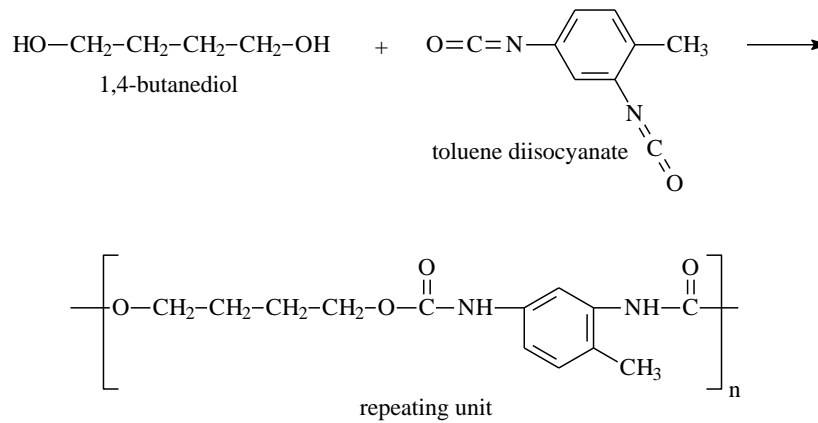
Example:



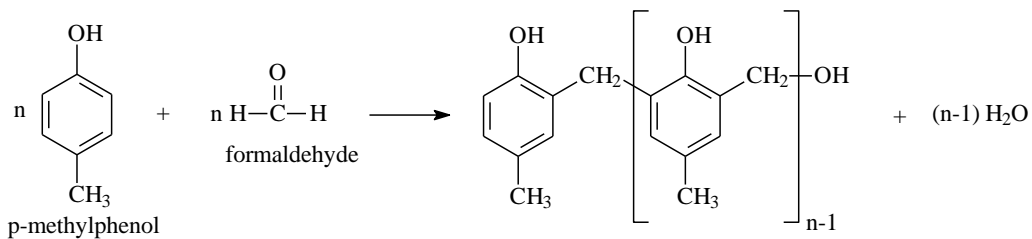
Example:



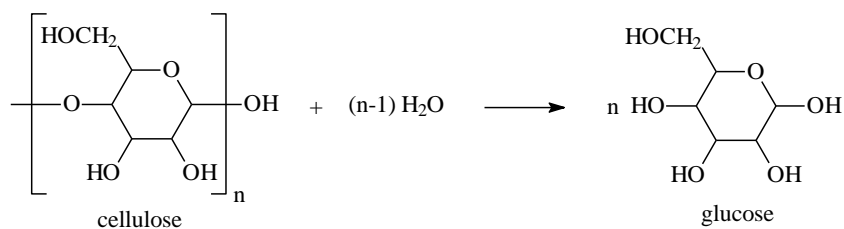
Example:



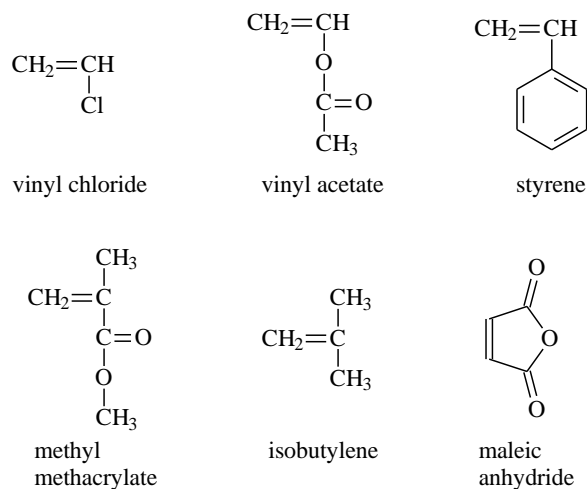
Example:



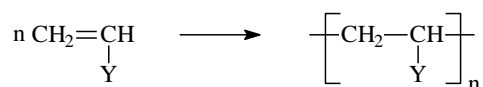
Carothers also classified certain naturally occurring polymers such as cellulose, starch, wool, and silk as condensation polymers, since they can be hypothesized to arise from the condensation of certain monomers, or conversely, their degradation can produce those monomers, with the gain or loss of a small molecule. For example, cellulose can be hydrolyzed to glucose. The reverse would be the hypothetical synthesis of cellulose by condensation polymerization.



Addition polymers were classified by Carothers as those formed from monomers without the loss of a small molecule. The major addition polymers are those formed by polymerization of monomers containing the carbon-carbon double bond.



These double bond containing monomers are converted to polymers via chain reactions involving radicals, anions, or cations, by which their double bonds are converted into saturated linkages.



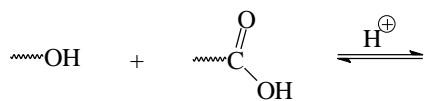
The Carothers classification system is not without its problems. The reaction of diols with diisocyanates to form polyurethanes (third example on p. PC3) clearly does not release any small molecule, but it should be obvious that they are structurally more similar to the condensation polymers than the addition polymers. Therefore we can state the following rule: a polymer is classified as a condensation polymer if its synthesis involves the elimination of small molecules, or it contains functional groups as part of the polymer chain, or its repeating unit lacks certain atoms that are present in the (hypothetical) monomer to which it can be degraded. If a polymer does not fulfill any of these requirements, it is classified as an addition polymer.

PSC 301
Problem Set 1

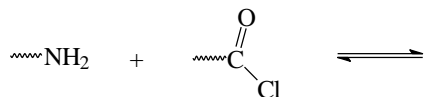
1. What are the two basic mechanisms, which have been proposed for nucleophilic aliphatic substitution, and how do their reaction kinetics differ?

2. Show the mechanism:

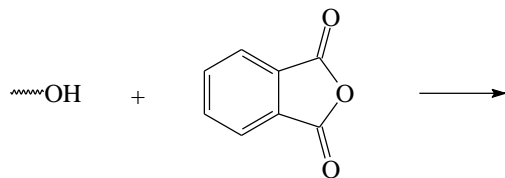
a.



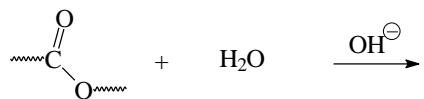
b.



c.



d.

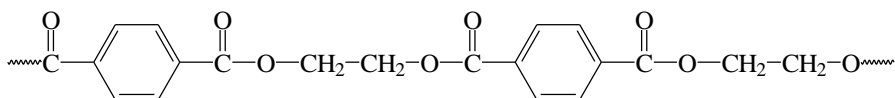


PSC 301

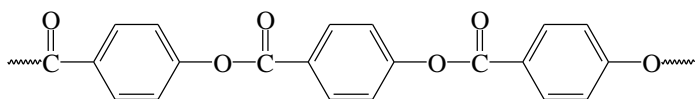
Problem Set 1 (page 2)

3. For each of the following polymer structures, identify whether the polymer is a condensation or addition polymer, identify the repeat unit and structural unit(s), and show structures of the monomer(s) from which the polymer could be derived.

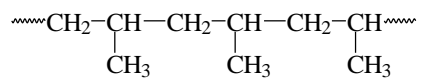
a.



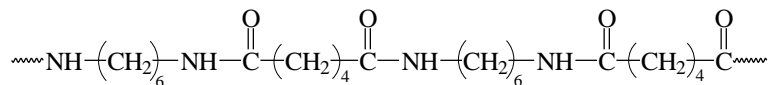
b.



c.



d.



2. Polymerization Mechanism

To address the shortcomings of the Carothers classification system, Paul Flory proposed to differentiate polymers on the basis of the polymerization mechanism by which they are formed. He classified polymerizations processes as either step growth and chain growth, with step growth corresponding largely to the condensation polymers and chain growth corresponding largely to the addition polymers. The following behaviors serve to compare the two basic processes.



Paul Flory

Step Growth

Reaction proceeds by the stepwise reaction between functional groups of monomer.
Any two molecules, regardless of size, may react if they carry appropriate functionality.
Molecular size builds steadily through dimer, trimer, tetramer, etc.
Large molecules are realized only toward the very end of the polymerization.

Chain Growth

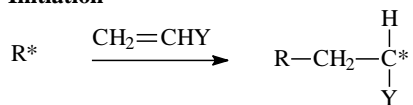
Reaction proceeds by propagation of a reactive center by the successive additions of large numbers of monomer molecules in a chain reaction.
Monomers can react only with the propagating center.
Requires an initiator species that contains a reactive center, e.g., a free radical.
Large molecules may be created very early in the polymerization.

The step growth process is characterized by the following series of reactions:

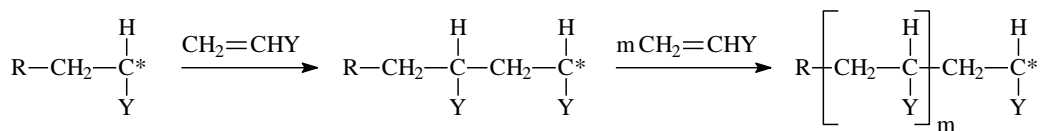
Monomer + monomer	→	dimer
Dimer + monomer	→	trimer
Dimer + dimer	→	tetramer
Trimer + monomer	→	tetramer
Trimer + dimer	→	pentamer
Trimer + trimer	→	hexamer
Tetramer + monomer	→	pentamer
Tetramer + dimer	→	hexamer
Tetramer + trimer	→	heptamer
Tetramer + tetramer	→	octamer
Etc.		

The chain growth process is characterized by the following reactions:

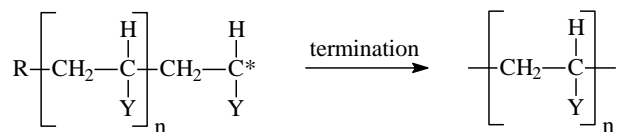
Initiation



Propagation

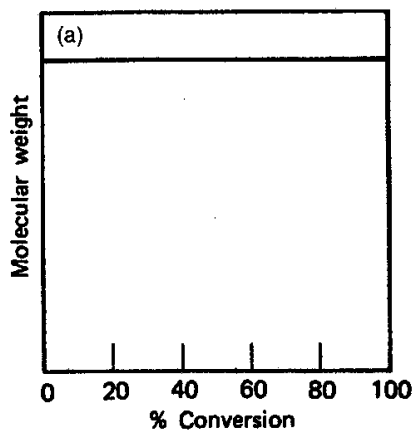


Termination

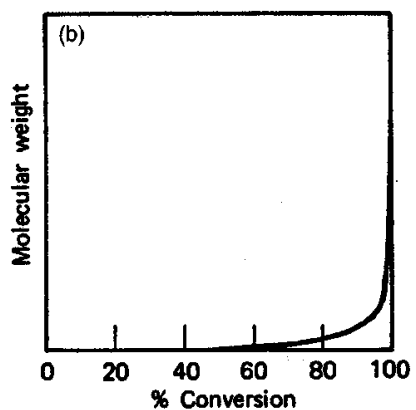


The following plots demonstrate the relationship between molecular weight of the polymer product as a function of % conversion of the polymerization reaction.

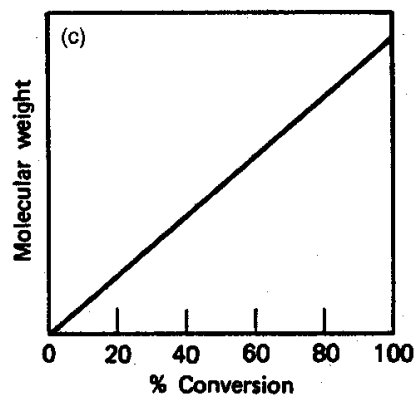
For chain growth, conversion is defined as the fraction of monomers that has been consumed.
 For step growth, conversion is defined as the fraction of functional groups that has been consumed.



Chain growth
(initiation slow relative to propagation;
termination operable)

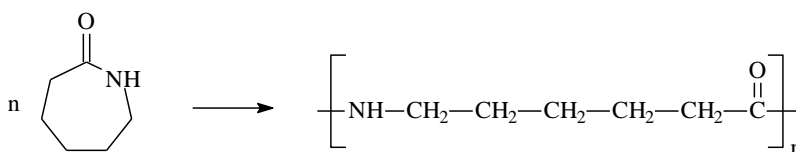


Step growth



Chain growth
(initiation fast relative to propagation;
no termination)

Ring-opening polymerizations of cyclic monomers typically proceed by a chain mechanism; although they produce polymer structures that resemble condensation polymers. In fact, the polymer shown below can also be made by condensation polymerization of the open-chain 6-aminocaproic acid.

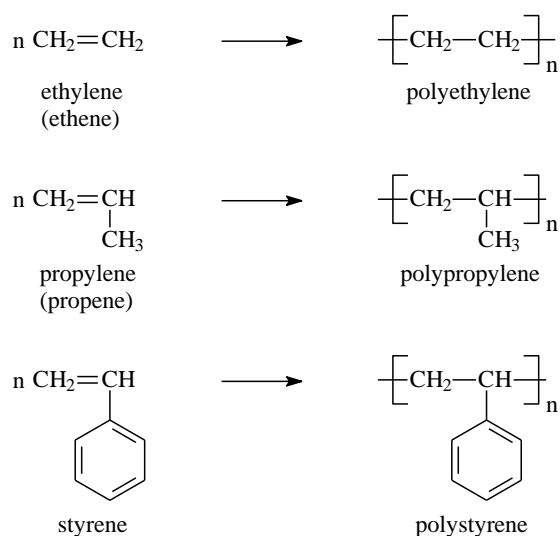


B. Nomenclature of Polymers

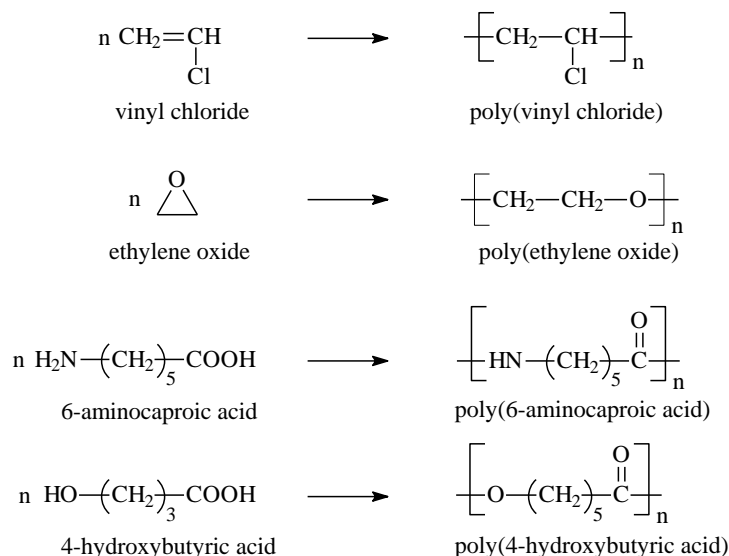
1. Nomenclature Based on Source

In this nomenclature system, the polymer is named according to the monomer from which it is derived. This system has the virtue of simplicity, but works well only for polymers derived from a single monomer. It is therefore widely used for polymers produced by chain growth (addition) and ring-opening polymerizations, and also for step growth polymerizations from a single monomer.

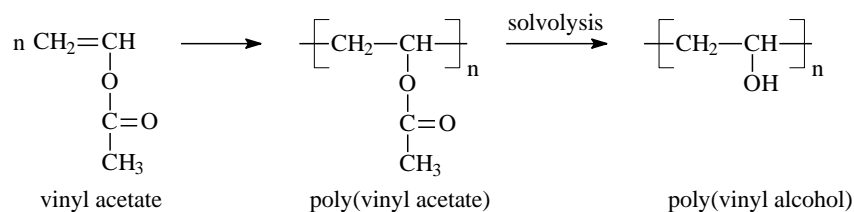
The polymer name is simply the monomer name with the prefix “poly” added without a space or hyphen. For example:



If the monomer has a substituted parent name or a multi-word name, the monomer name is enclosed in parentheses and the prefix “poly” is added. For example:

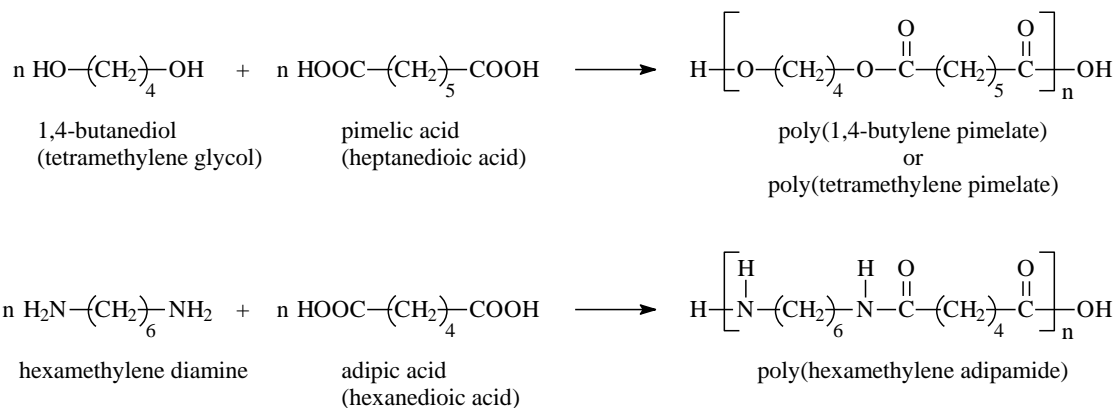


Occasionally a polymer is named from a source that is strictly hypothetical. For example, poly(vinyl alcohol) is actually made by the hydrolysis or solvolysis (with methanol) of poly(vinyl acetate). The monomer vinyl alcohol cannot be isolated for polymerization, since it exists only as the minor component within the keto/enol tautomer pair, acetaldehyde/vinyl alcohol ($K = [\text{enol}]/[\text{keto}] \approx 3 \times 10^{-7}$).



2. Nomenclature Based on Structure (Non-IUPAC)

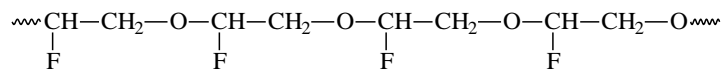
This semi-systematic nomenclature system is commonly used for condensation polymers synthesized from two different monomers, particularly polyesters and polyamides. In analogy to the naming of small-molecule esters and amides, the polymer is named by following the prefix “poly” with parentheses enclosing the name of the bivalent group derived from the glycol or diamine followed by the name of the dicarboxylic acid with appropriate suffix, that is, *-ate* for ester and *amide* for amide. The following examples will illustrate the system.



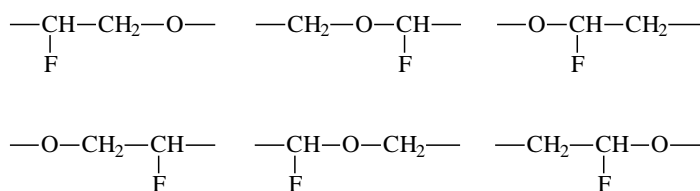
3. IUPAC Structure-Based Nomenclature System

The IUPAC structure-based nomenclature system provides a unique name for any single-strand polymer (as opposed to a ladder polymer). It is based on identification and naming of a preferred constitutional repeating unit (CRU). The CRU is the smallest possible repeating unit of the polymer, and it is a divalent unit for a single strand polymer. The name of the polymer is given by the prefix “poly” followed by the name of the CRU in parentheses or brackets.

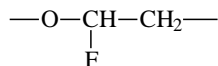
For example, consider the following polymer:



It has six possible CRU's:

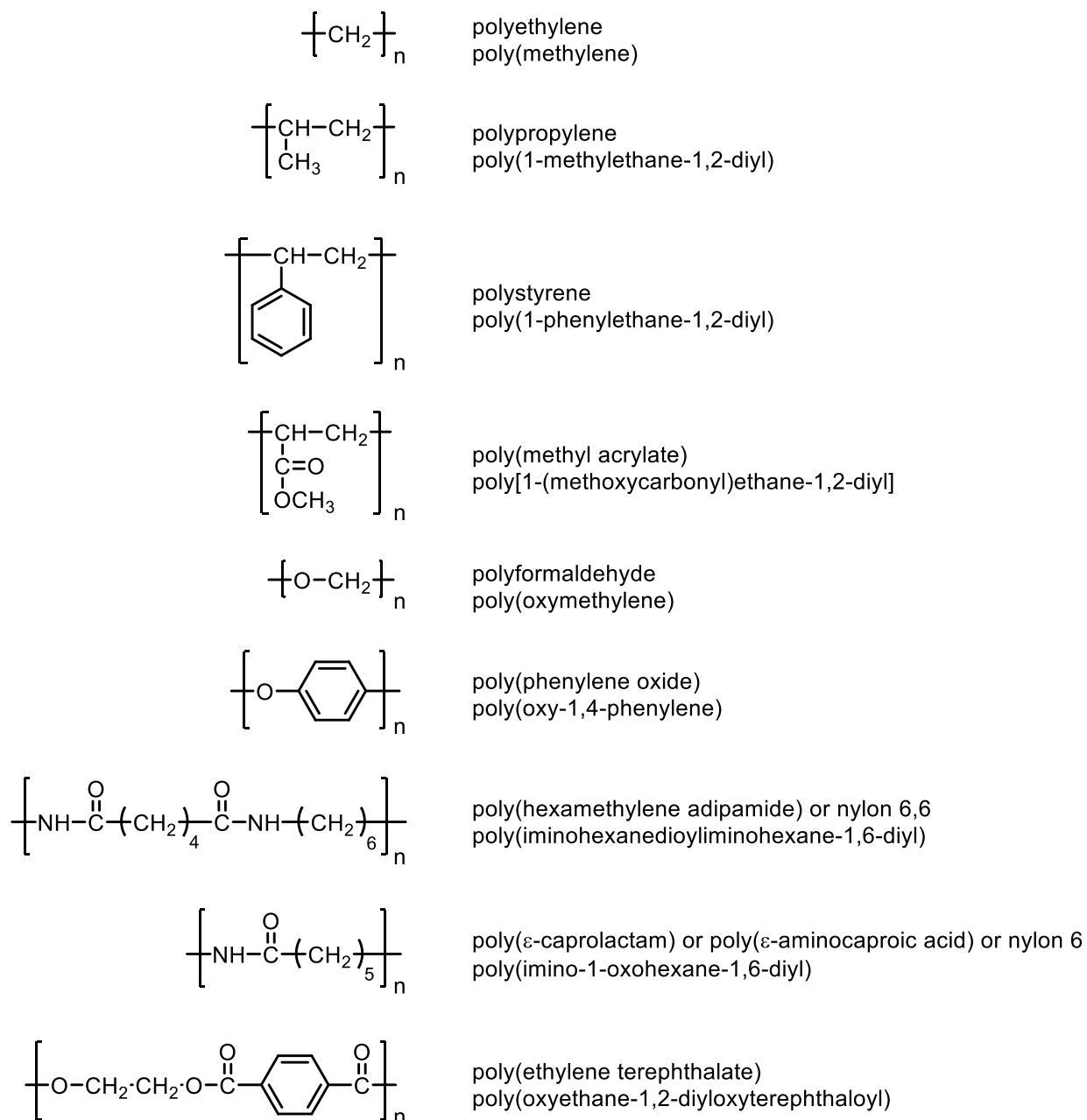


But, according to the IUPAC priority rules (see Odian, pp. 12-14), the correct CRU is,



and the correct IUPAC name is poly(oxy-1-fluoroethylene)

The following examples from the “Purple Book” (<https://iupac.org/what-we-do/books/purplebook/>) help to further illustrate that IUPAC nomenclature system. In each case the IUPAC name is shown below the more established source or semisystematic structure-based name.



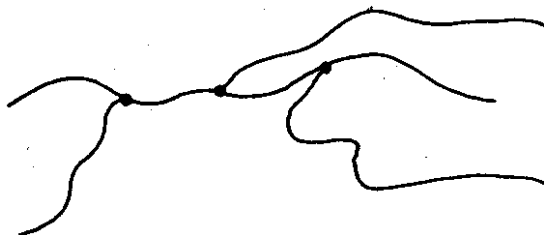
4. Trade Names and Non-Names

Over the years, the naming of polyamides according to DuPont's original commercial naming scheme, has come to be used generally by the polymer community. This naming scheme applies only to polyamides derived from unbranched, aliphatic diamines and diacids. According to this scheme, the polyamide is named as "nylon x,y" where x is the number of carbon atoms in the diamine monomer, and y is the number of carbon atoms in the diacid monomer. Thus the polyamide derived from hexamethylene diamine and adipic acid is named nylon 6,6. If the polyamide is derived from a single monomer, such as 6-aminocaproic acid, it is named "nylon z" where z is the number of carbon atoms in the monomer.

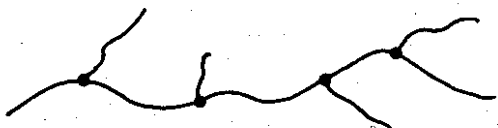
C. Linear, Branched, and Crosslinked Polymers



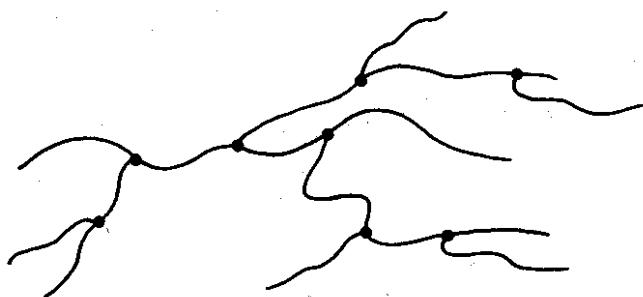
Linear



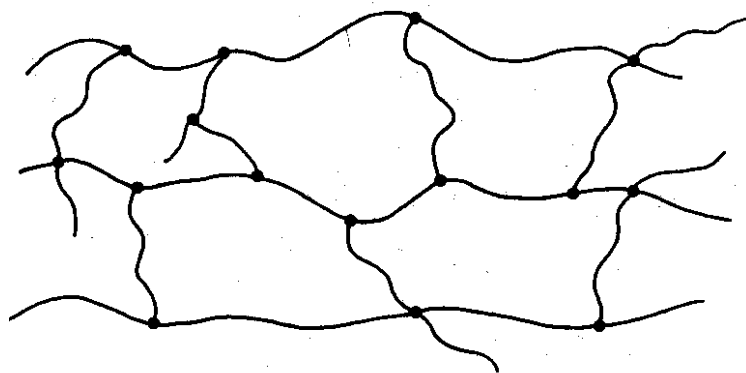
Long-Chain Branched



Short-Chain Branched
(Comb-like)



Arboreal or hyperbranched



Crosslinked

D. Molecular Weight

In the following two sections on molecular weight, a variable denoted by a capital letter will signify an absolute quantity, and a variable denoted by a lower case letter will signify a fractional quantity.

1. Number Average Molecular Weight

The number average molecular weight of a polymer sample is obtained by methods, such as colligative property measurements, that count the number of molecules in the polymer sample. Number average molecular weight, \overline{M}_n , is defined as the total weight of all the molecules in the sample, $\sum W_x = W$, divided by the total number of moles in the sample, $\sum N_x = N$. The variable x is simply the summation index (it serves to distinguish the terms of the summation).

$$\overline{M}_n = \frac{W}{N} = \frac{\sum N_x M_x}{\sum N_x}$$

N_x = number of moles (mol) of polymer molecules within a given size group

M_x = molecular weight (g/mol) of the polymer molecules of a given size group

Note that: $W_x = N_x M_x$

Example: A polymer sample is composed of three size groups or fractions.

Fraction	Weight of fraction, W_x (g)	Moles of fraction, N_x (mol)	Molecular weight of fraction, M_x (g/mol)
A	2	1×10^{-3}	2,000
B	3	6×10^{-4}	5,000
C	2	2×10^{-4}	10,000

$$\sum W_x = 7 \text{ g}$$

$$\sum N_x = N_1 + N_2 + N_3 = \frac{2}{2,000} + \frac{3}{5,000} + \frac{2}{10,000} = 1.8 \times 10^{-3} \text{ (mol)}$$

$$\sum N_x M_x = N_1 M_1 + N_2 M_2 + N_3 M_3 = \frac{2}{2,000} \text{ (mol)} \times 2,000 \text{ (g)} + \frac{3}{5,000} \times 5,000 + \frac{2}{10,000} \times 10,000 = 7 \text{ (g)}$$

$$\overline{M}_n = \frac{\sum N_x M_x}{\sum N_x} = \frac{7 \text{ (g)}}{10^{-3} + 6 \times 10^{-4} + 2 \times 10^{-4} \text{ (mol)}} = 3,889 \text{ (g/mol)}$$

2. Weight Average Molecular Weight

The weight average molecular weight, \overline{M}_w , of a polymer sample is obtained by light scattering, which is sensitive not to the number of molecules but rather to their size. Weight average molecular weight is defined as:

$$\overline{M}_w = \sum w_x M_x = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

where, w_x is the weight fraction of molecules with molecular weight M_x .

Example: Using the same polymer above, composed of three size groups or fractions,

$$\sum w_x M_x = \frac{2}{7} \times 2,000 \text{ (g/mol)} + \frac{3}{7} \times 5,000 + \frac{2}{7} \times 10,000 = 5,571 \text{ (g/mol)}$$

3. Molecular Weight Distribution (Polydispersity Index)

\overline{M}_n and \overline{M}_w represent the first and second moments of the distribution of molecular weights of a polymer sample. Therefore, $\overline{M}_w \geq \overline{M}_n$. The breadth of the distribution of molecular weights within a polymer sample is generally referred to as the molecular weight distribution (MWD) or polydispersity index (PDI) and is defined as,

$$\text{MWD} = \frac{\overline{M}_w}{\overline{M}_n}$$

PSC 301**Problem Set 2**

1. A sample of polystyrene is composed of a series of fractions of different-sized molecules. Calculate number average and weight average molecular weight and molecular weight distribution:

Fraction	Weight of Fraction	Molecular Weight
A	0.10	12,000
B	0.19	21,000
C	0.24	35,000
D	0.18	49,000

2. A company manufactures four sizes of ball bearings: 5, 8, 12, and 15 mm diameter. The mean weight of a single bearing of each size is, respectively: 5, 20, 70, 135 g. Monthly production is as follows:

Diameter (mm)	Bearings Produced (x 1000)
5	50
8	100
12	80
15	20

Calculate the number and weight average diameter of bearings produced within a month.

3. Works problems 1-1 through 1-5 on p. 37 of Odian's book (p. 38 in 3rd Edition).

E. Physical State of Polymers

1. Crystalline and Amorphous Behavior

Typical low molecular weight compounds are crystalline solids at lower temperatures but possess a well-defined melting point, above which they exist as an amorphous (without order) liquid or melt (e.g., adipic acid, a compound discussed earlier, displays a melting point of 152°C). The higher the molecular weight of the compound and/or the stronger the intermolecular interactions, the higher will be the viscosity of the liquid state. In contrast, many polymers at lower temperatures display a physical state, or morphology, that is partially crystalline and partially amorphous; the crystalline and amorphous portions usually exist as phase-separated domains (microscopic volume elements). Such polymers are described as semi-crystalline. Crystallinity imparts toughness, strength, and solvent resistance to polymers. The presence of crystallinity in a polymer is most reliably detected using x-ray scattering. Some polymers are completely amorphous at lower temperatures, but because of their high molecular weight, they appear to be solids. But this is an illusion, and flow can often be detected at longer time scales. Completely crystalline polymer are rarely encountered.

Single polymer crystals grown from solution consist of folded-chain platelets or lamella, in which the polymer chain axes have been shown to be perpendicular to the plane of the platelet (parallel to the smallest dimension of the platelet). This situation can only be reasonably explained by assuming that the chains fold back and forth on themselves in an accordion-like manner during crystallization. It has been proposed that the folds occur either by adjacent re-entry or non-adjacent (switchboard) re-entry. When polymers crystallize from the melt, chain folding also occurs, and larger, spherical structures are observed to grow outward from a point of nucleation; these structures are termed spherulites.

2. Determinants of Polymer Crystallinity

The extent of polymer crystallinity is determined by polymer structure. Crystallinity is favored by chains that are able to quickly and easily pack into the crystalline state. In general chains should be structurally regular, compact, streamlined, and moderately flexible. This allows the chains to rapidly crystallize from the melt, for example, during an injection molding process. Polyethylene, polyoxymethylene, and poly(ethylene oxide) are examples of highly crystalline polymers that achieve their high degrees of crystallinity primarily through these attributes. Crystallinity is also favored in polymers possessing strong secondary bonding forces between chains, such as hydrogen bonding found in polyamides. Intermolecular hydrogen bonding is especially favorable toward crystallization. However, to create an intermolecular hydrogen bond, the NH group of one chain must index properly with the CO group of a neighboring chain. This “indexing” requirement lessens crystallization kinetics and ultimately the degree of crystallinity. In spite of this, polyamides show significant crystallinity, and moreover, crystallinity in polyamides can be significantly increased by the process of mechanical drawing (stretching) at a temperature below the melt temperature (so-called “cold drawing”). Polymers with bulky side groups, for example, polystyrene, poly(methyl methacrylate), and polymers with rigid cyclic groups in the main chain, for example poly(ethylene terephthalate), show low crystallization tendencies. Some chains, such as those of natural rubber, are so very flexible that they are unable

to stay aligned long enough to crystallize; however, they do show the phenomenon of strain-induced crystallization.

3. Thermal Transitions

Polymers display two major types of thermal transitions, a crystalline melting point, T_m , and a glass transition temperature, T_g . The T_m is the temperature at which the crystalline domains of a semi-crystalline polymer melt. Completely amorphous polymers do not display a T_m and only display a T_g . The T_g is the temperature above which the amorphous domains are soft and rubbery and below which they are hard and glassy. The T_m is always higher than the T_g .

4. Applications of Polymers

The mechanical properties of polymers, shown below in terms of their characteristic stress-strain plots, largely determine the applications for which they are used.

