Introduction to Polymerization Processes

Reference:

Aspen Polymers: *Unit Operations and Reaction Models,*
Aspen Technology, Inc., 2013.

1- Polymer Definition

A polymer is a macromolecule made up of many smaller repeating units providing linear and branched chain structures. Although a wide variety of polymers are produced naturally, synthetic or man-made polymers can be tailored to satisfy specific needs in the market place, and affect our daily lives at an ever-increasing rate. The worldwide production of synthetic polymers, estimated at approximately 100 million tons annually, provides products such as plastics, rubber, fibers, paints, and adhesives used in the manufacture of construction and packaging materials, tires, clothing, and decorative and protective products.

2- Polymer Manufacturing Process Steps

Polymer manufacturing processes are usually divided into the following major steps:

- Monomer Synthesis and Purification
- Polymerization
- Recovery / Separation
- Polymer Processing

The four steps may be carried out by the same manufacturer within a single integrated plant, or specific companies may focus on one or more of these steps. The polymerization step is usually the most important step in terms of the economic viability of the manufacturing process. The desired outcome for this step is a polymer product with specified properties such as:

- Molecular weight distribution
- Melt index
- Composition
- Crystallinity/density
- Viscosity

Polymerization processes may be batch, semi-batch or continuous. In addition, they may be carried out in bulk, solution, slurry, gas-phase, suspension or emulsion.

In the polymerization step, the reactions which occur usually cause dramatic changes in the reaction medium (e.g. significant viscosity increases may occur), which in turn make several important issues such as high conversion kinetics, residence time distribution, agitation and heat transfer difficulties.

3- Polymer Structure

Synthetic polymers are produced when *monomers* bond together through polymerization and become the repeating structure or *segment* within a chain. When two or more monomers bond together, a polymer is formed. Small polymer chains containing 20 or less repeating units are usually called *oligomers*.

The fact that identifiable segments are found repeatedly along a polymer chain, provides convenient ways to categorize polymers. Polymers can be classified based on segment composition or sequence:

- Homopolymers - containing one type of repeating unit which can be mapped into one segment
- Copolymers - which have two or more repeating units. Copolymers can be in a random, alternating, block, or graft configuration
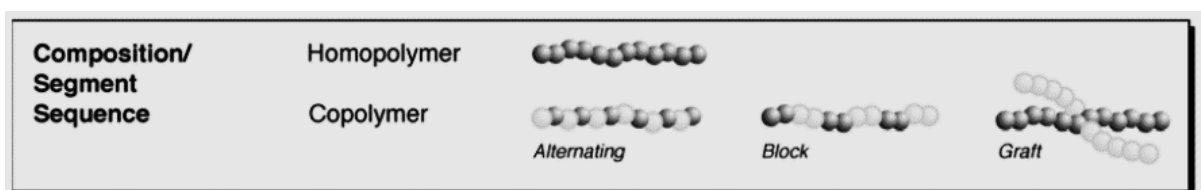
If we consider the arrangement of a given chain, another classification arises. Polymers may be:
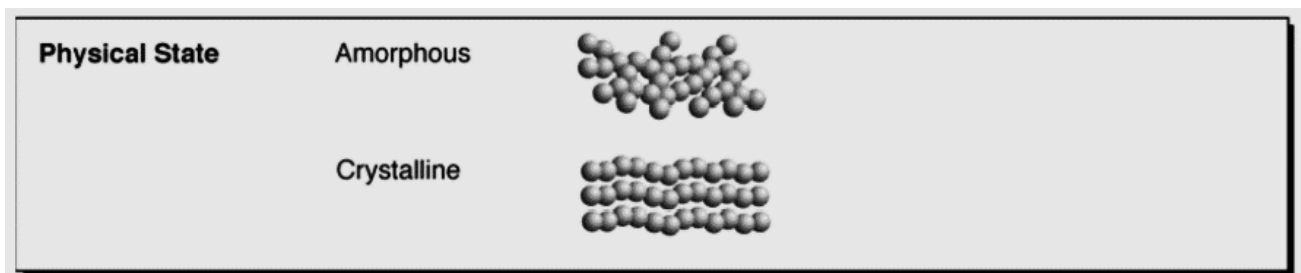
- Linear

- Branched (with short or long chains)

- Star

- Ladder

- Network

Chain Structure	Linear	
	Branched	Short / Long
	Star	
	Ladder	
	Network	
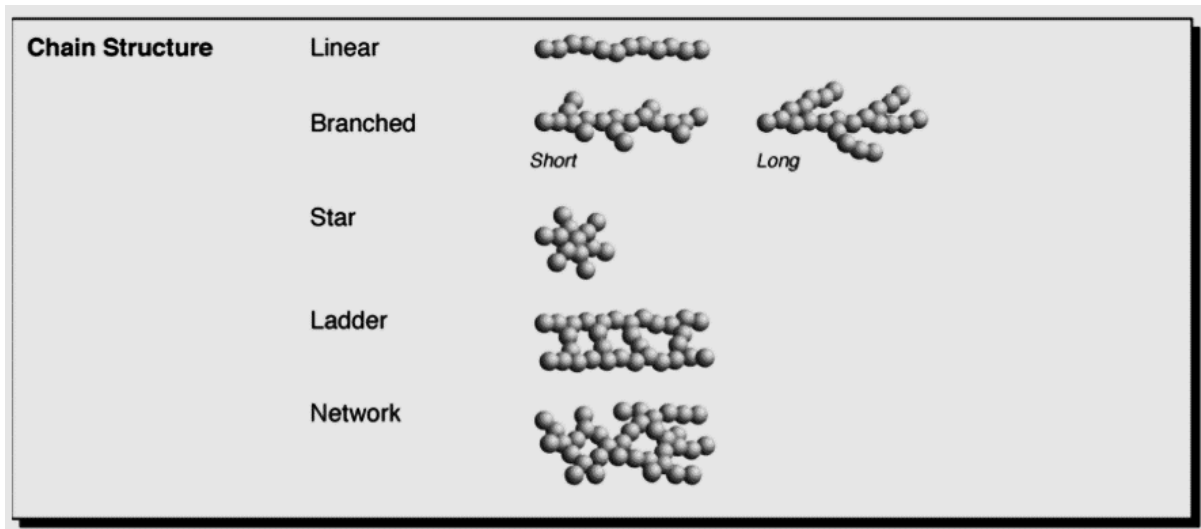
Another classification that results from polymer structure has to do with physical state. A solid polymer may be:

- Amorphous - when the chains are not arranged in a particular pattern
- Crystalline - when the chains are arranged in a regular pattern

Physical State	Amorphous	
	Crystalline	

Polymers can classified based on the type of atoms exist in their backbone to homochains and heterochains.

Homochains produced through chain-growth polymerization, have only carbon atoms on the polymer backbone.

Heterochains produced through step-growth polymerization have other types of atom incorporated into the polymer backbone.
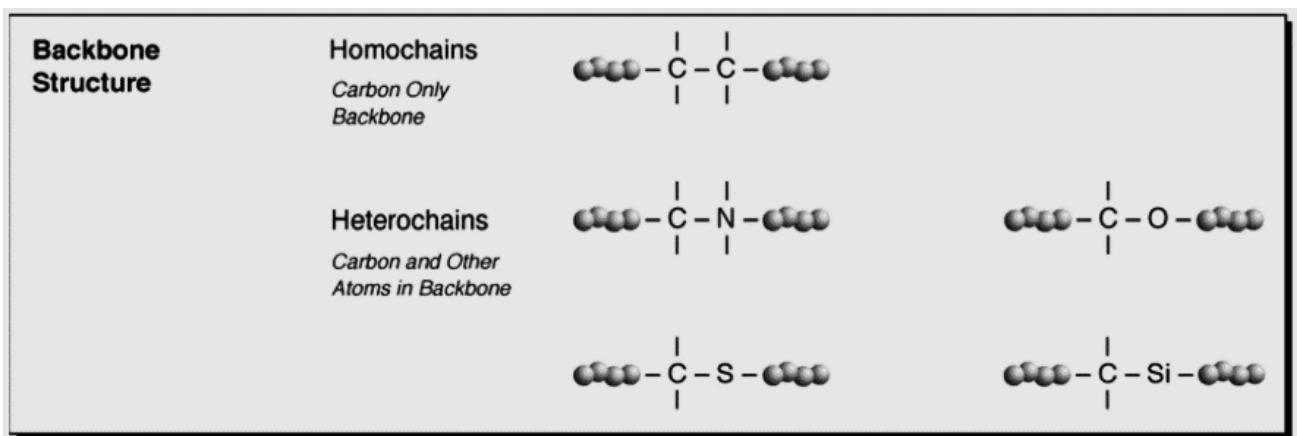
Polymer Category	Description	Examples
Polymers with carbon-carbon backbone		
Polyacrylics	Ethylene backbone with one acrylic acid (or derivative) as side group per ethylene	Polyacrylic acid, polymethyl methacrylate, polyacrylonitrile, polyacrylamide
Polydienes	One double bond per repeat unit	Polybutadiene
Polyhalogen hydrocarbons	Fluorine or chlorine side group per ethylene	Polyvinyl fluoride, polyvinylidene fluoride, polyvinylchloride,
Polyolefins	Alphatic or aromatic substituents	Polyethylene, polypropylene, polyisobutylene, polystyrene
Polyvinyls	From vinyl monomers	Polyvinyl acetate, polyvinyl alcohol
Polymers with carbon-nitrogen backbone		
Polyamides	Amide group on backbone	Nylon 6, nylon 6,6
Polyurethanes	Urethane group on backbone	Polyurethane foams
Polyureas	Urea group on backbone	Polyurea resins

Polymer Category	Description	Examples
Polymers with carbon-oxygen backbone		
Polyacetals	Acetal group on backbone	Polyacetate
Polyethers	Ether group on backbone	Polyethylene oxide, polyphenylene oxide
Polyesters	Ester group on backbone	Polycarbonate polyethylene therephthalate, polybutylene therephthalate polylactide
Polymers with carbon-sulfur backbone		
Polysulfides	Sulfide group on backbone	Polysulfide fibers

A related classification divides polymers by thermal and mechanical properties into:

- Thermoplastics (may go from solid to melt and vice versa)
- Thermosets (remain solid through heating)
- Elastomers (which have elastic properties)

Finally, polymers can be categorized based on the form they are manufactured into: plastics, fibers, film, coatings, adhesives, foams, and composites.

4- Component Categories

When developing a simulation model in Aspen Polymers (formerly known as Aspen Polymers Plus), users must assign components present in process flow streams to one of the following categories:

- Conventional
- Polymer
- Oligomer
- Segment
- Site-based

The following figure illustrates the different categories of components and their input requirements:
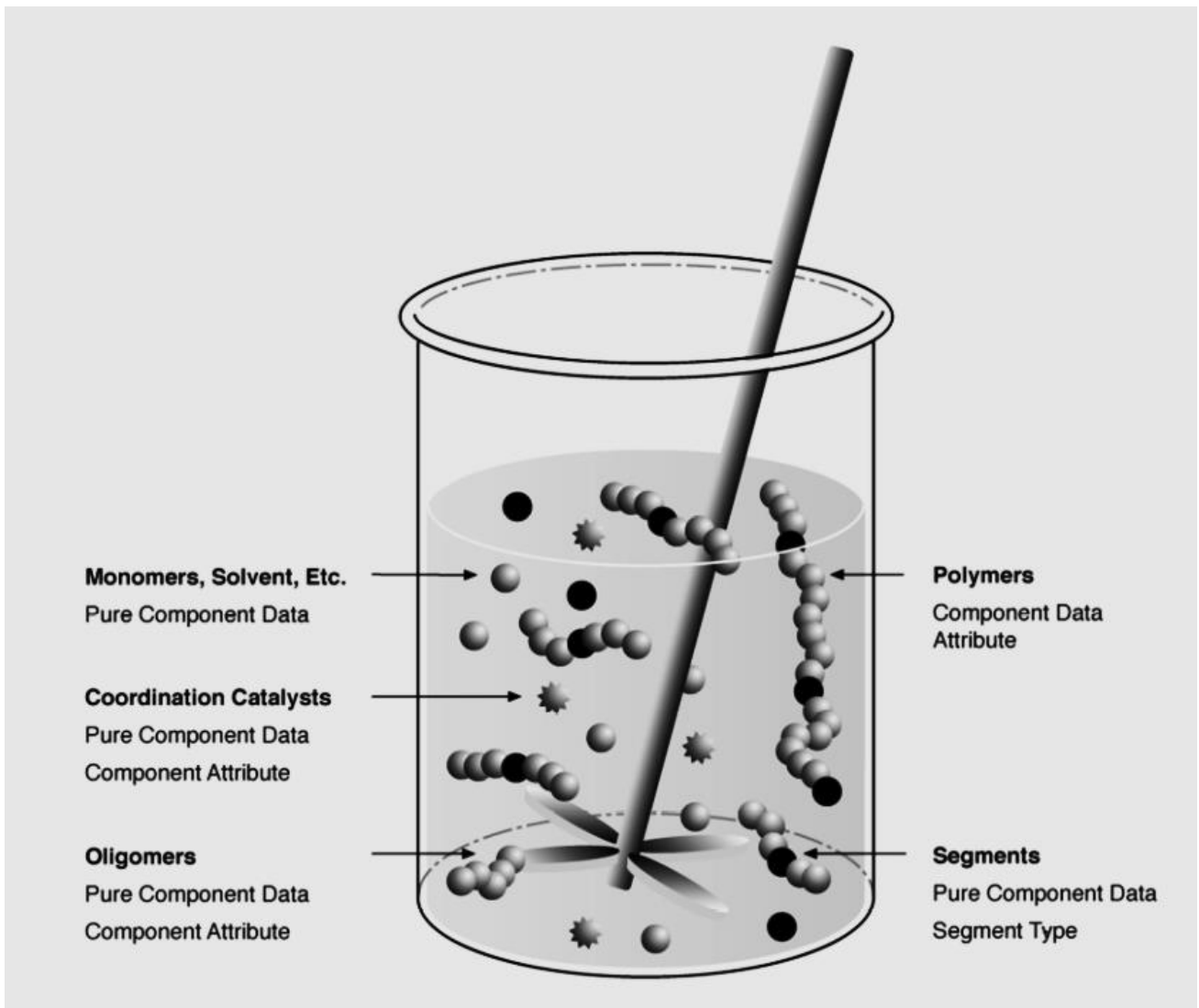
Conventional Components

Standard conventional components are molecular components such as water. These components have a fixed molecular structure and participate in phase equilibrium. Components falling into this category include:

- Monomers
- Initiators
- Chain transfer agents
- Solvents
- Catalysts

In order to fully specify conventional components, you need only specify pure component data required for the phase equilibrium calculations. This data may be entered or retrieved from component databanks (such as PURE databank).

Note: Ziegler-Natta catalysts and ionic initiators require additional characterization information.

In the Pure Component databank, components are named using a nomenclature developed for Aspen Plus. Each component is given an alias summarizing the number of each type of atom: C, H, O, N, P, S, CL, F, etc. (e.g. C2H4 for ethylene). For cases where the same alias matches several components, a counter is added to make the distinction (e.g. C2H4O2-1 for acetic acid).

Polymers

In Aspen Polymers, polymer components represent a distribution of polymeric species. The average size and composition of the molecules in this distribution can change throughout the simulation. Each polymer molecule is considered to be made up of repeating units or segments. Typically, the segments correspond to the monomers that are used to grow the polymer.

The structure of polymers depends on the number and type of segments they contain and the arrangement of segments in linear, branched, or cross-linked forms.

Component attributes are used to track polymer structural properties such as:

- Segment composition
- Copolymer composition and average sequence length
- Degree of polymerization
- Molecular weight
- Branching
- Moments of molecular weight distribution

- Molecular architecture (physical arrangement of segments within the polymer molecule)

Segments are specified independently from polymers. For each polymer, you must select the types of component attributes to be included in the simulation model. Data for polymers are retrieved from the POLYMER databank.

The Polymer Databank does not follow the conventional nomenclature. The polymer aliases are the typical acronyms used in industry or academia, and the polymer names consist of the repeat unit name enclosed in parentheses and preceded by the prefix Poly (e.g. PS or POLY(STYRENE) for polystyrene).

Note: The MW property parameter used to store molecular weights in the component databanks is the true molecular weight for all component types except polymers. For polymers, the true polymer molecular weight is normally tracked as a component attribute only. The molecular weight stored in the databank is the apparent molecular weight calculated as the average segment molecular weight.

Oligomers

By convention, oligomers are defined as components with two or more segments and a fixed molecular structure. They can be defined as volatile or non-volatile. Typically, the oligomer feature is used to allow users to track the loss of volatile short-chain polymers.

In order to specify oligomers, you must specify their composition in terms of the number and type of segments they contain. Oligomers do not require component attributes. For this reason, you may treat a polymer as an oligomer in cases where you want to process the polymer within a unit operation model which cannot handle polymer component attribute data.

Data for oligomers are retrieved either from the pure component databank or from the POLYMER databank.

Segments

Segments are the structural units of a polymer or oligomer and are specified independently from these components. Their structure is fixed throughout a simulation. Segments typically correspond to the monomers used to grow the polymer. They are divided into types depending on their location on the polymer chain:

- Repeat units
- End groups
- Branch point (attached to three or four branches)

Data for segments are retrieved from the SEGMENT databank. In the Segment Databank, a segment name comes from the name of the monomer from which it originates. Therefore, in this databank component names and aliases follow the same conventions as those for the Pure Component Databank. A label is added to the monomer name to identify the segment as either a repeat unit,-R, an end group,-E, or a branch point, -B (e.g. for butadiene segments: C4H6-R-1or BUTADIENE-R-1 corresponding to the repeat unit –CH2–CH=CH–CH2–, C4H5-E-1 or BUTADIENE-E-1 corresponding to the end group –CH=CH–CH=CH2 and C4H5-B or BUTADIENE-B corresponding to the branch segment —CH₂—CH=CH—CH<).

Initiators

The INITIATO databank contains data for initiator components. Rate constants in this databank are derived from half-life data in vendor datasheets published on public web sites. These datasheets generally contain data at several temperatures, allowing the activation energy and prefactor to be determined. These rate constants depend on the reaction environment, and may vary between polar and non-polar solvents. Where multiple sets of data were available, the data from monomer or organic solvents were used in preference to data from aqueous solutions. Molecular weight and other parameters are calculated from structure using estimation methods from Aspen Plus, except in those few cases where vapor pressure data was provided in the datasheets.

In the INITIATO databank, components are named using industry-standard acronyms. Each component is given an alias summarizing the number of each type of atom: C, H, O, N, P, S, CL, F, etc. For cases where the same alias matches several components, a counter is added to make the distinction (e.g.–1,-2, etc).

Segment Methodology

The segment approach to characterizing components is a fundamental methodology which affects almost every functionality within Aspen Polymers. Segments are used as the building blocks for polymers. Once you have specified the types of segments in the polymer, the segment composition and degree of polymerization defined as component attributes may be used to define the size and composition of the polymer.

For oligomers, although component attributes are not used, the number of each segment must be specified directly.

Most of the Aspen Polymers physical property models calculate polymer and oligomer properties from segment properties. This is done by taking into account the degree of polymerization and the segment composition. The calculated properties should be the same for both oligomers and polymers, assuming that the oligomer structure and molecular weight were specified correctly. Note that this is true for mass-based properties only. Mole-based properties will be different between polymer and oligomer if their apparent molecular weights are different.

Within the polymerization reaction models, segments also play a key role. As polymerization progresses, the models map the reacting monomers into the corresponding segments and return rates of change for the segment composition.

5- Structural Properties

Polymer properties fall into many categories:

- Structural properties

- Thermophysical properties - which provide an indication of the thermodynamic behavior of polymers
- Thermochemical properties - which provide information on thermal stability
- Transport properties
- Processing and end-use properties - which provide information about processability and performance during end-use

Polymer structural properties do not provide a direct measure of the performance of the polymer product during processing or during its end use. However, there is a relationship between polymer structural properties and the end use properties. For this reason, it is important to account for such properties within polymer process simulation models.

Structural Properties as Component Attributes

Component attributes provide a convenient framework to associate structural characterization data to components in a flow stream. They are carried throughout the flowsheet along with state and composition information, and effectively extend the stream structure.

Aspen Polymers uses component attributes as a vehicle for tracking important modeling information for polymers, ionic initiators and Ziegler-Natta catalysts. For example, there are component attributes to store:

- Segment composition (segment fraction or segment flow)
- Copolymer composition and average sequence length
- Degree of polymerization (number, weight, and z-average)
- Molecular weight (number, weight, and z-average)
- Degree of branching (long and short)
- Degree of cross-linking (cross-link density)
- Molecular architecture (physical arrangement of segments within the polymer molecule)

- Live polymer properties
- Aggregate polymer properties

In the case of multi-site-type Ziegler-Natta catalyst polymerization, the attributes provide the structure to store the properties by site. Examples of catalyst attributes include the fraction of dead and potential sites. The catalyst attributes are used to track catalyst activity. There are also component attributes available to track user defined data.

Component attributes are divided into classes to reflect the nature of various structural properties carried in process streams:

- Class 0 component attributes are derived quantities from other attributes. They are therefore recalculated from these attributes after they are updated. For example, number average degree of polymerization is a Class 0 component attribute. It is computed from the zeroth and the first moments of chain length distribution.
- Class 1 component attributes are structural properties per unit mass. They are not used for polymers.
- Class 2 component attributes are structural properties per unit time. Examples are zeroth and first moments of chain length distribution

Structural Property Distributions

The common polymer structural properties for which distributions are typically considered include:

- Chain size - molecular weight or chain length
- Copolymer composition
- Degree of branching
- Polymer particle size

In order to accurately characterize a polymer component, and maintain control of polymer product properties, engineers must concern themselves with these distributions.

From a modeling standpoint, many theoretical and empirical functions have been developed to represent distributions. These functions tend to fall into categories derived from their formulation, or from their graphical representation.

Distributions that mimic the normal bell-shaped graphical representation are called unimodal distributions. This is in contrast with distributions that reveal several peaks and are called bimodal or multimodal distributions. The following figure shows examples of unimodal and bimodal distributions.
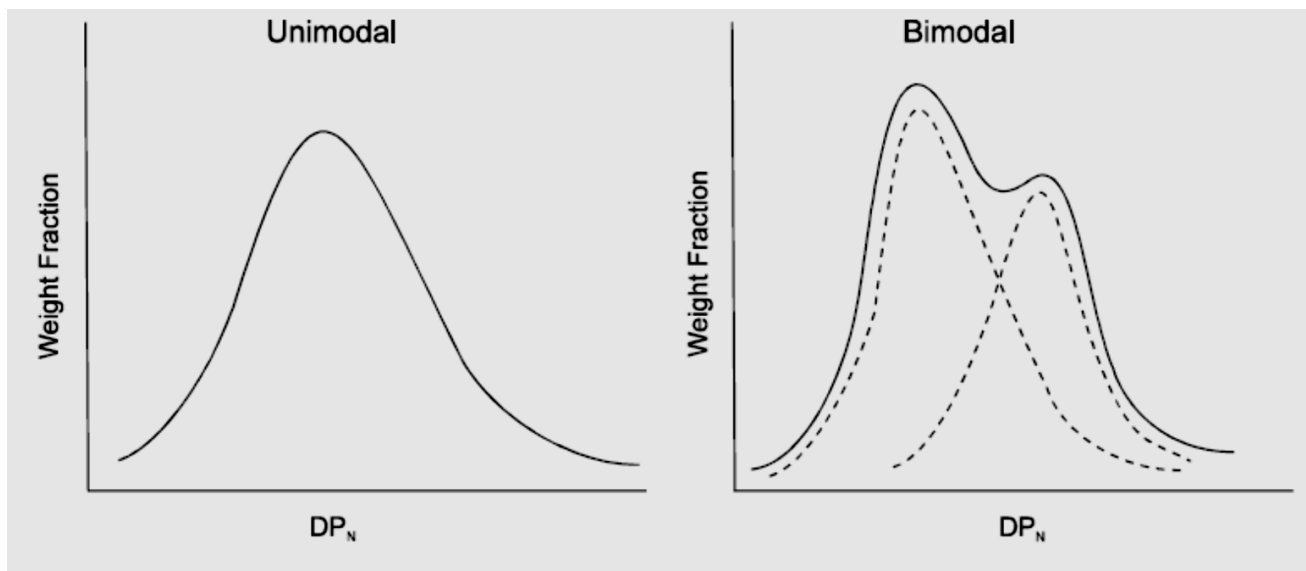
There is a great demand to know the full molecular weight distribution, particularly for complex distributions that may have a shoulder, or are even bimodal. This information is needed for optimization of rheological and mechanical properties of the final polymer product.

Within Aspen Polymers a dual approach for determining polymer properties is used:

- Method of moments continues to be the preferred approach for calculating average properties.
- Method of instantaneous properties is used to calculate distributions. This method addresses the issue of data storage and computational complexity in tracking distributions.

The instantaneous distribution functions are unimodal. However, the distribution functions for polymer accumulated in a multi-reactor system may be multimodal.

Method of Moments

For a given property s, the property distribution may be described by a frequency function f_s when the property is a discrete variable, and by a density function $f(s)$ when the property s is continuous. Therefore, f_s and $f(s)$ represent the portion (for example, number, weight and, volume fraction) of the population whose property is exactly s (discrete) or whose property lies between s and $s + ds$.

Distribution moments may be defined from the origin of the average property, i.e. property is equal to 0, or from the mean value of that property. The moments employed in Aspen Polymers use the first approach. In this case, the generalized form of the relationship between distribution moment and distribution function is shown below:

$$\mu_k \equiv \begin{cases} \sum_{all\ s} s^k f_s & \text{for the frequency function} \\ \int_{all\ s} s^k f(s)\,ds & \text{for the density function} \end{cases}$$

Where:

μ = Moment

k = Moment order (e.g. 0-3 for zeroth through third moment)

s = Property value (e.g. chain length, molecular weight, particle size, etc.)

The average properties can be calculated as ratios of the moments. Number average is the ratio of first to zeroth moment, μ_1/μ_0. Weight or Volume average is the ratio of second to first moment, μ_2/μ_1. Z-average is the ratio of third to second moment, μ_3/μ_2.

For the case of chain length distribution the moment frequency distribution is given by:

$$\lambda_m = \sum n^m Q_n$$

Where:

λ = Moment

m = Moment order

n = Chain length or degree of polymerization

Q_n = Number of moles of polymer of length n

The average chain length properties are then:

DP_n (Number average degrees of polymerization) = λ_1/λ_0

DP_w (Weight average degrees of polymerization) = λ_2/λ_1

DP_z (Z average degrees of polymerization) = λ_3/λ_2

DPI (Polydispersity index) = $DP_w/DP_n = \lambda_2\lambda_0/\lambda_1^2$

In Aspen Polymers, the average molecular weight values are determined using the average degree of polymerization and average segment molecular weight.

Method of Instantaneous Properties

Applying the method of moments for the calculation of property distributions has several drawbacks. In addition to CPU requirements and computational complexity, a larger number of moments than currently calculated would be required. Knowledge of leading moments of a distribution does not permit one to unambiguously construct a

complex distribution. One must therefore look beyond the method of moments for a more powerful method to predict these complex distributions.

A better approach for generating molecular weight distributions consists of storing reaction rate data throughout the kinetic calculations, and later using them to construct the full distribution of polymer accumulated in the reactor system. Such an approach was developed by Hamielec (Hamielec, 1992) as follows:

$$W(r) = (\tau + \beta)\left\{\tau + \frac{\beta}{2}(\tau + \beta)(r-1)\right\}r.\exp\left\{-(\tau + \beta)r\right\}$$

Where $W(r)$ is the instantaneous weight chain length distribution and

$$\tau = \frac{R_{td} + R_f}{R_p}, \quad \beta = \frac{R_{tc}}{R_p}, \quad r = \text{chain length}$$

R_p = Propagation rate

R_{td} = Rate of termination by disproportionation

R_{tc} = Rate of termination by combination

R_f = Total rate of chain transfer to small molecules (not polymers)

In other words, $W(r)$ is the weight chain length distribution of dead polymer chains produced in a small time interval t to $t+dt$, in a batch reactor. $W(r)$ is also the weight chain length distribution of dead polymer chains produced in a CSTR operating at steady-state. For the case of CSTRs in series, the end product polymer distribution is a composite that is a weighted average of the distributions of polymer produced in each reactor. A plug flow reactor can be divided into several volume elements and treated as a series of CSTRs.

The method of instantaneous properties assumes that polymer molecules grow and deactivate quickly as the growing center terminates or moves to another molecule of monomer, solvent, or chain transfer agent. The method assumes that the polymer molecules are conserved once they are formed. These assumptions limit the method of instantaneous properties to addition polymerization (ionic polymerization and step-

growth condensation reactions are specifically excluded because these reaction schemes are reversible). Further, the assumption that polymer molecules are conserved once they are formed can be invalid in the presence of certain side reactions, including random (thermal) scission, which destroys polymer molecules, and chain transfer to polymer, which causes inactive polymer molecules to become active again, leading to long-chain branch formation and significantly increasing the weight-average molecular weight and PDI. The molecular weight distribution charts display the MWW and PDI calculated by the method of moments and the method of instantaneous properties. If the predicted values for the MWW and PDI are not in reasonable agreement with each other, it is most likely due to these types of side reactions.

6- Polymerization Reactions

Over the years, many classifications have been developed for polymerization reactions. One classification divides them into *condensation* and *addition* polymerization.

Condensation polymerization results in the elimination of a smaller molecule, water for example, through the reaction of bi- or polyfunctional monomers.

Addition polymerization, on the other hand, does not produce small molecule byproducts. The repeating units within the polymer have the same structure as the monomers from which they originated.

The problem with this classification is that while it describes differences in the molecular structure of the resulting polymer, it does not fully capture the differences in the reaction mechanism.

A classification that is more useful for capturing the difference in the mechanisms through which polymers are produced divides polymerization reactions into *step-growth* and *chain-growth* polymerization. The differences between step-growth and chain-growth polymerization are summarized in the following tables:

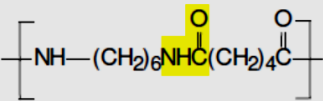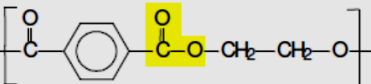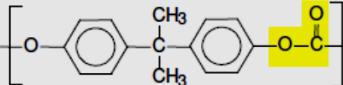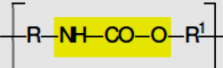|	Step Growth Polymerization	Chain Growth Polymerization
Monomer type	Bi-, polyfunctional	No functionality
Reaction categories	Single intermolecular reaction	Several consecutive reactions for initiation, growth, and termination
Reacting species	Any combination of monomers, oligomers, polymer chains	Monomers and active centers (free-radical, ion, polymer, catalyst end)
Elimination product	Small molecule elimination product for condensation polymerization only	None
Polymer growth rate	Slow, chain lifetime of the order of hours	Rapid, chain lifetime of the order of seconds
Polymer size	High molecular weight at high conversion	High molecular weight at all conversion levels

Reaction Type	Active Center	Initiation	Growth Reaction
Step Growth			
Condensation	Bi-, polyfunctional end groups	None	Nucleophilic substitution
Pseudo condensation	Bi-, polyfunctional end groups	None	Nucleophilic addition
Ring Scission	Bi-, polyfunctional end groups	Yes for ring opening	Nucleophilic addition or substitution
Chain Growth			
Free-radical	Free radical	Chemical, thermal, radiative	Monomers add on to radical
Coordination	Metal complex	Catalyst activation	Monomers insert into metal complex carbon bond
Ionic	Anion or cation	Dissociation	Monomers add on at ion pair

Step-Growth Polymerization

Step-growth polymerization retains the definition given for condensation polymers for the majority of cases. That is, monomers react with each other to eliminate small molecules. Step-growth polymers are formed through the same reaction type occurring

between functional groups located on any combination of monomers, oligomers, or polymer chains. The polymer chains continue to grow from both ends as polymerization progresses. The reactions occur at a relatively slow rate and chains grow slowly.

Step-growth polymerization can be sub-categorized as *condensation*, *pseudocondensation*, and *ring-opening* or *ring-scission* depending on the chemical pathways through which the reactions occur. The following table lists typical commercial step-growth polymers:

Polymer (Trade Name)	Monomers	Repeat Unit	Reaction Type	Applications (Similar Polymers)
Polyamide (Nylon 6,6)	Adipic acid Hexamethylene diamine	—NH—(CH₂)₆NHC(CH₂)₄C—	Dicarboxylic acid + diamines	Fiber, plastics (Lycra, Nylon 6)
Polyester (PET)	Terephthalic acid Ethylene glycol	C—◯—C—O—CH₂—CH₂—O—	Dicarboxylic onhydride + glycols	Fiber (PBT, Dacron, Nylon)
Polycarbonate (Lexan)	Bisphenol-A Phosgene	O—◯—C(CH₃)(CH₃)—◯—O—C	Dihydroxy reactant + Phosgene	Lenses, packaging (Merlon)
Polyurethane	Toluene diisoyamate polyether diol	—R—NH—CO—O—R¹—	Diisocyanate + dialcohol	Foam, packaging

Chain-Growth Polymerization

Chain-growth polymers are formed through the addition of monomers to an active center (free-radical, ion, or polymer-catalyst bond), in a "chain" reaction, at a very fast rate. Furthermore, several different types of reaction occur to initiate, propagate, and terminate polymer growth.

Chain-growth polymerization can be categorized as *free-radical*, *coordination complex*, or *ionic*, depending on the type and method of formation of the active center. The following table lists typical commercial chain-growth polymers:

Polymer	Monomers	Repeat Unit	Reaction Types	Applications
Polyethylene	Ethylene	$\begin{bmatrix} CH_2-CH_2 \end{bmatrix}$	Bulk/solution (free-radical) Coordination complex (Ziegler-Natta)	Film, packaging
Polystyrene	Styrene	$\begin{bmatrix} CH_2-CH \\ C_6H_5 \end{bmatrix}$	Bulk/solution/suspension (free-radical)	Containers, packaging, insulation
Polypropylene	Propylene	$\begin{bmatrix} CH-CH_2 \\ CH_3 \end{bmatrix}$	Coordination complex (Ziegler-Natta)	Films, packaging, autoparts, sealants
Polyisobutylene	Isobutylene	$\begin{bmatrix} CH_3 \\ C-CH_2 \\ CH_3 \end{bmatrix}$	Ionic	Films, plastic tubing
Polyvinyl chloride	Vinyl chloride	$\begin{bmatrix} CH_2-CH \\ Cl \end{bmatrix}$	Bulk/solution/suspension (free-radical)	Floor coverings, pipes
Polymethalmethacrylate	Methyl Methacrylate	$\begin{bmatrix} CH_3 \\ CH_2-C \\ COOCH_3 \end{bmatrix}$	Bulk/solution (free-radical)	Lenses, plastics
Styrene butadiene rubber	Styrene Butadiene	$\begin{bmatrix} CH_2-CH-CH_2-CH=CH-CH_2 \\ C_6H_5 \end{bmatrix}$	Emulsion (free-radical)	Tires, belting, shoe soles

Step Growth Reaction Sub-classes

In addition to chemical pathways, the environment or process conditions in which the polymerization reactions occur introduce more sub-classes of polymers. For example, step-growth reactions may take place as *melt phase*, *solid-state*, *solution*, or *interfacial* polymerization:

- *Melt-phase processes* are carried out above the melting point of the polymer
- *Solid-state processes* are carried out below the melting point of the polymer
- *Solution processes* are carried out in the presence of an inert solvent
- *Interfacial processes* are carried out in the interface between an organic phase and an aqueous phase

Chain Growth Reaction Sub-classes

Chain-growth polymerization may take place in *bulk phase*, *solution*, *precipitation*, *suspension*, or *emulsion*:

- *Bulk polymerization* is carried out in the bulk monomer phase without a solvent
- *Solution polymerization* is carried out in the presence of an inert solvent in which monomers and polymer are dissolved
- *Precipitation polymerization* is carried out using a solvent to precipitate out the polymer
- *Suspension polymerization* involves monomers suspended as droplets in a continuous phase (usually water) to which an oil-soluble initiator is added
- *Emulsion polymerization* involves monomers and micelles dispersed in a continuous water phase using surfactants. Initiator is added to the emulsion of partially water soluble monomers in the surfactant solution

Built-in Models in Aspen Polymers

The polymerization reaction models available in Aspen Polymers are summarized in the following table:

Model Name	Chemistry	Processes	Polymers
Step-growth			
STEP-GROWTH	Step-growth condensation	Melt phase, solution, interfacial	PC, PBT, PET, Nylons
SEGMENT-BAS	Step-growth addition	Melt phase, solution, interfacial	Polyurethanes, polyimides, PPO, engineering plastics
Chain-growth			
FREE-RAD	Free-radical	Bulk, solution	PS, PVAC, SAN, PMMA
EMULSION	Free-radical	Emulsion	SBR, SBA
ZIEGLER-NAT	Ziegler-Natta / metallocene coordination complex	Bulk, solution	HDPE, PP, LLDPE
IONIC	Anionic/Cationic group transfer	Solution	PIB, SBR, PEO
Generic			
SEGMENT-BAS	Segment-based power-law reaction model	N/A	PVA from PVAC