

Free Radical Polymerization

Reference:

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

1. Introduction

The free-radical bulk/solution polymerization model is applicable to bulk and solution polymerization processes. Some examples of applicable polymers are:

- General purpose polystyrene - Made by polymerization of styrene monomer with or without solvent fed continuously to reactor.
- High impact polystyrene - Made by polymerization of an unsaturated rubber dissolved in styrene in a solution process. Also produced in suspension processes.
- Poly(vinyl chloride) - Produced in bulk polymerization using monomer soluble free radical initiators. Most of the homopolymers and copolymers of vinyl chloride, however, are produced by suspension polymerization.
- Poly(vinyl acetate) - Produced industrially by the polymerization of vinyl acetate in bulk or solution processes. Also produced in suspension and emulsion processes. Both batch and continuous processes are used.
- Poly(methyl methacrylate) - The vast majority of commercially prepared acrylic polymers and methacrylic polymers are copolymers. Commercially they are prepared by solution polymerization. They are also produced by emulsion and suspension polymerization.
- Low density polyethylene - Made by high pressure, free radical processes in either a tubular reactor or a stirred autoclave. Typical commercial processes include staged compression, initiator injection, partial conversion of ethylene to polymer, separation of ethylene from polymer, extrusion of molten polymer, and cooling of ethylene.

Bulk and solution polymerization processes are characterized by the fact that the reactions proceed in a single phase. Typically, the monomers are fed to a reactor with or without a solvent. A small amount of initiator is also fed. At the reaction temperature, the initiator decomposes to form radicals that initiate the polymerization reactions. The polymer formed is usually soluble in the monomer/solvent mixture.

However, in some systems, such as PVC, the polymer is insoluble and forms a separate phase. The most commonly used reactor types include batch, semi-batch, continuous stirred-tank and tubular reactors. Flowsheets consisting of several reactors in series are common. The main technical challenges with bulk/solution polymerization processes are heat removal, handling of the highly viscous liquid, and recovery of residual monomer/solvent. Several modes of heat removal can be employed, including jacket cooling, internal cooling coils/baffles, external heat exchangers and reflux condensers.

The Free-Radical model may also be used to simulate suspension polymerization processes in which the polymer is completely soluble in the organic (monomer) phase. Two reaction models can be applied together to represent reactions in each liquid phase. An example of this process is: production of Poly(styrene) in a continuous suspension process in a series of CSTR type reactors.

2. Reaction Kinetic Scheme

Most free-radical polymerizations have at least four basic reaction steps:

- Initiation
- Propagation
- Chain transfer to another molecule (i.e. monomer, solvent, polymer or transfer agent)
- Termination

These reactions occur simultaneously during the polymerization. For branched polymers additional reactions for long and short chain branching can also be present. A comprehensive kinetic scheme for the free-radical homo- and copolymerization of up to N_m monomers has been built into Aspen Polymers. The scheme includes most of the reactions commonly used for modeling free radical polymerization. The model also includes several optional reactions:

- Terminal double bond polymerization
- Pendent double bond polymerization (for diene monomers)
- Head-to-head propagation (for asymmetric monomers)
- Cis- and trans- propagation (for diene monomers)
- Primary and secondary decomposition of bifunctional initiators

Reactions such as depropagation and random chain scission are not included in the current model.

2.1. Polymer Chain Terms

The term *live polymer chain*, $P_n[i]$, refers to growing polymer chains containing n segments, with a radical attached to a segment of type i , i.e., segment formed from monomer i . The term *dead polymer chain*, D_n , refers to terminated polymer chains that do not have an attached radical. The term *bulk polymer chain* is used to refer to the sum of the live and dead polymer chains. The subscript n refers to the chain length in terms of the number of segments or monomer units incorporated in the polymer chain. Live chains are reactive and can participate in the polymerization reactions while dead chains are usually considered inert, except when long chain branching reactions are important (such as terminal double bound polymerization).

The radical attached to one end of a live polymer chain is considered to be mobile and moves away from the initiator fragment with every addition of a monomer molecule. It is believed that after a few monomer additions the chemistry of the initiator fragment and developing chain microstructure will not have a strong influence on the mode of monomer addition.

The free-radical kinetic model assumes that the reactivity of a live polymer chain depends only on the active segment containing the radical, and is independent of the polymer chain length and other structural properties. For example, in the propagation reaction, the rate of propagation, R_{pij} , is independent of the polymer chain length. It

depends only on the concentration of monomer j and the concentration of live polymer chains with active segments of type i . Models using this assumption are referred to as *terminal models* in the polymerization literature.

The rate constants for each reaction in the built-in kinetics is calculated at the reaction temperature and pressure using the modified Arrhenius equation shown below with user specified parameters: pre-exponential (or frequency) factor, activation energy, activation volume, and reference temperature:

$$k = k_o \exp \left[\left(\frac{-Ea}{R} - \frac{\Delta VP}{R} \right) \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] f_g \quad (1)$$

Where:

k_o = Pre-exponential factor in 1/s for first order reactions, and $m^3/(kmol s)$ for second order reactions

Ea = Activation energy in mole-enthalpy units

ΔV = Activation volume in volume/mole units

P = Reaction pressure

R = Universal gas constant

T_{ref} = Reference temperature

f_g = Gel effect factor from optional built-in or user-defined gel effect correlation

The second term in the exponential function contains an activation volume that is important for high pressure polymerization systems. For low to moderate pressures, the activation volume is typically set to default value of zero. This term is used to account for the pressure dependence of the reaction rate constant.

The free-radical model allows the rate expression to be modified by a gel effect term, f_g . The gel effect term can be calculated using one of several built-in correlations or it can be calculated by an optional user-defined gel effect subroutine.

2.2. Initiation

The initiation step involves the generation of reactive free-radicals followed by the addition of a monomer molecule (chain initiation) to form chain radicals of unit length, $P_1[i]$. The non-chain or primary radicals (R^*) may be generated by the thermal decomposition of a chemical initiator, a catalyzed initiation reaction involving electron transfer from ions, or by thermal/radiation induced mechanisms. Three types of standard initiation reactions are included in the built-in kinetics:

- Initiator decomposition reaction
- Induced initiation reaction
- Catalyzed initiation reaction

The initiator decomposition reaction accounts for primary radical generation from the thermal decomposition of chemical initiators.

The induced initiation reaction can be configured to account for the generation of radicals by thermal and radiation induced mechanisms from the monomers themselves, with or without the use of a coinitiator or promoter.

The catalyzed initiation reaction can be used to account for redox initiation, which has found wide application in aqueous emulsion polymerization systems.

Initiator decomposition reaction

The most commonly used radical generation method is the thermal decomposition of chemical initiators (usually peroxide or azo compounds) which decompose to form radicals when heated to an appropriate temperature. Only small amounts of the chemical initiator (less than 1 wt. % based on monomer) are needed.

The initiator decomposition reaction is modeled as a first order thermal decomposition reaction:



Where:

C_I = Initiator concentration

k_d = Initiator decomposition rate constant

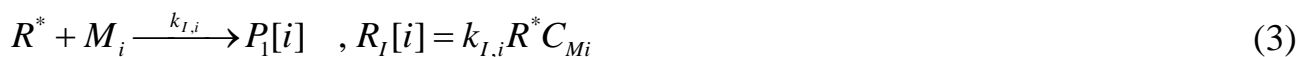
ε = Initiator efficiency

N = Number of produced primary radicals (1 or 2)

A and B = By-product molecules

Primary chain initiation

The reactive primary radicals (R^*) react with monomer by the primary chain initiation reaction to form polymer chain radicals of unit length, as shown below:



Where:

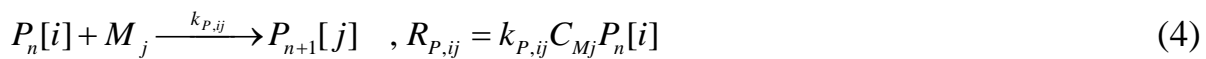
C_{M_i} = Concentration of monomer of type i

$k_{I,i}$ = Chain initiation rate constant

The chain radicals grow by successive addition of monomer molecules to form long chain polymer molecules. It is common practice to set the chain initiation rate constants equal to the propagation rate constant of each monomer.

2.3. Propagation

The chain radicals grow or propagate by the addition of monomer molecules to form long polymer chains of length n , $Pn[i]$. The propagation reaction is represented by:

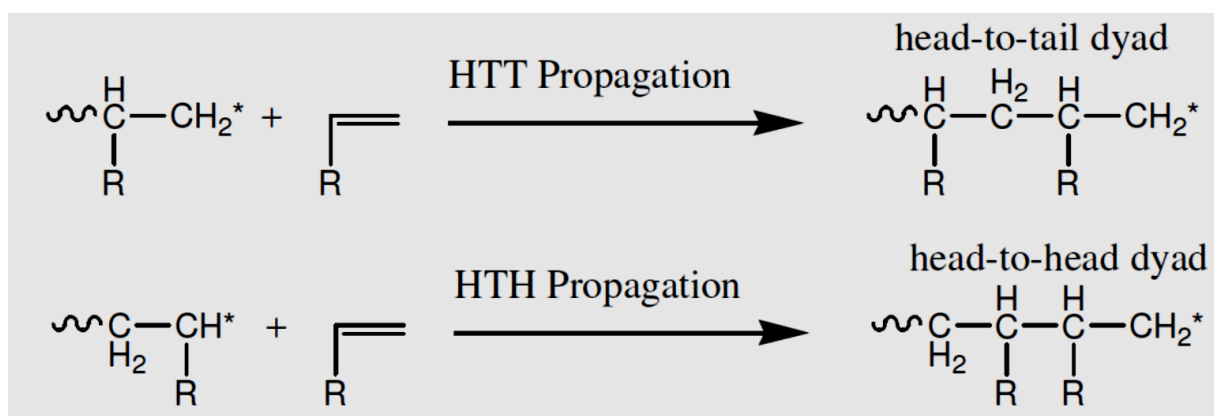


where monomer j is being added to a polymer chain of length n , with an active segment of type i . The resulting polymer chain will be of length $n+1$ and the active segment will be of type j . The active segment type usually represents the last monomer incorporated into the polymer chain.

For copolymerization, there will be (no of monomers)² propagation reactions having different reactivities. For example, with two monomers, four reaction exist with four rate constants (k_{P11} , k_{P12} , k_{P21} , k_{P22}) where the first subscript refers to the active segment type while the second subscript refers to the reacting monomer type.

Head-to-Head Propagation

When reactions occur between substituted vinyl monomers or 1,3 dienes, the repeat units usually join the chain in a head-to-tail configuration, as shown below (here HTT = head-to-tail). A portion of the monomers may join the chain in the head-to-head configuration, as shown in the second reaction below. Head-to-head unions can also result from termination by combination as described later.



The head-to-head dyads disturb the normal regularity of the chain. As a result, the head-to-head fraction of the polymer can have a strong influence on the crystallinity of the polymer, and thus influence the mechanical properties of the final product.

The model can track head-to-head additions using the optional HTH Propagation reaction. The polymer attributes HTHFLOW and HTHFRAC (head-to-head flow and fraction) must be included in the list of attributes on the Polymers, Polymers subform. The model does not explicitly track normal head-to-tail additions. Instead, the standard propagation reaction is used to track the total (head-to-head and head-to-tail) propagation rate. The head-to-head propagation reaction explicitly tracks the head-to-head propagations. This design allows the user to fit the overall propagation rate first, and then refine the model by adding head-to-head additions.

2.4. Chain transfer

Chain transfer to small molecules such as monomer, solvent or chain transfer agent usually involves the abstraction of hydrogen from the small molecule by the chain radical and leads to the termination of the live chain. At the same time, a new primary transfer radical is formed which can start chain polymerization. The effect of chain transfer on the polymerization kinetics depends on the reactivity of the transfer radical. When the transfer radical is very reactive, as is the case when the chain initiation rate constant is greater than the propagation rate constant, chain transfer will not lower the polymerization rate or conversion, but will reduce the molecular weight of the polymer. However, if the transfer radical is less reactive than the monomer based propagating radical, as in the case of low chain initiation rate constant, both the conversion and molecular weight of the polymer will be lowered.

Chain transfer to solvent or agent

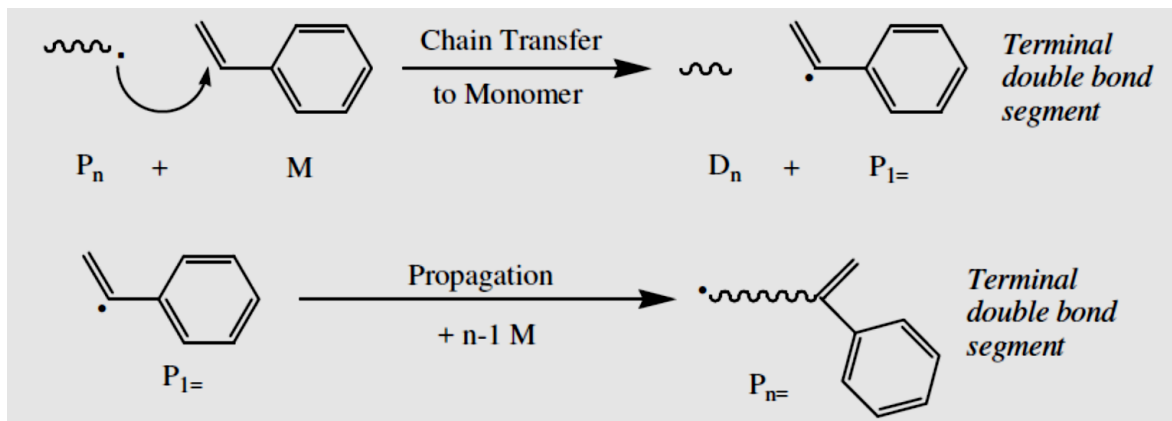
Chain transfer to solvent and chain transfer to a transfer agent have the following rate expressions:



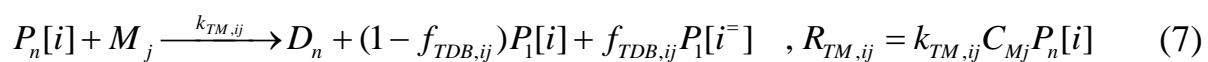
For transfer to agent or solvent the transfer radicals are assumed to have the same reactivity as the primary radicals formed by initiation.

Chain transfer to monomer – Generation of terminal double bonds

In the chain transfer to monomer reaction, the live polymer end P_n abstracts a hydrogen from a monomer molecule, resulting in a dead polymer chain D_n . The monomer, which loses a hydrogen, becomes a live polymer end group with an unreacted double bond $P_1[i^=]$. Subsequent propagation reactions generate long-chain polymer radicals with a terminal double-bond segment at the opposite end of the chain $P_n^=$. These initial reaction steps are shown below:



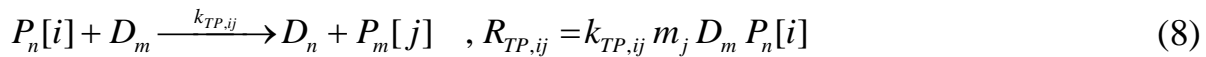
The chain transfer to monomer reaction does not always generate a terminal double bond. The terminal segment may undergo a re-arrangement reaction, which destroys the double bond site. The model parameter “TDB fraction, $f_{TDB,ij}$ ” can be used to specify the fraction of chain transfer to monomer reactions that generate a terminal double bond. The reaction rate of the chain transfer to monomer reaction is defined as:



Chain transfer to polymer

The radical in one polymer chain can transfer to a repeat unit in a second polymer chain. This *chain transfer to polymer* reaction always generates a long chain branch,

since subsequent propagation from the live site causes the backbone molecule to grow a new branch. The chain transfer to polymer reaction can be written as:



Where m_j represents the number of repeat groups of type j in the molecule to which the radical is transferred.

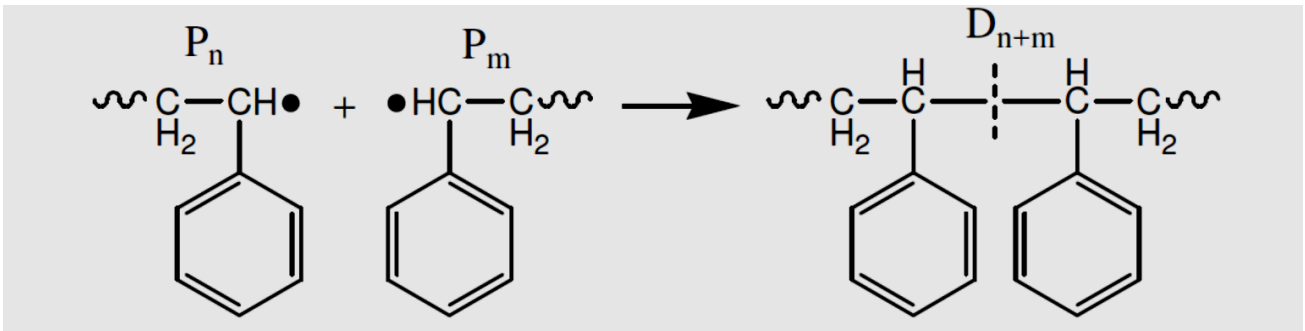
Each transfer reaction generates one long chain branch. The optional polymer component attributes **LCB** and **FLCB** are used to track the molar flow rate of long chain branches and the long chain branching frequency (branch point per thousand repeat units).

2.5. Termination

Intermolecular termination occurs by one of two mechanisms, *combination (coupling)* and *disproportionation*. Many monomers (e.g. MMA) show both types of termination while other monomers (e.g. styrene) terminate predominantly by combination. The mode of termination has a strong influence on the average polymer chain length and chain length distribution, especially when chain transfer is not significant. When the combination reaction is dominant, the polydispersity (in a single CSTR) will approach 1.5. The polydispersity approaches 2.0 when disproportionation is dominant.

Termination by combination

In termination by combination, two live polymer end groups react with each other, forming a single dead chain with a head-to-head segment pair. Each of these reactions, on average, doubles the molecular weight of the polymer. The figure below shows an example for poly(styrene).



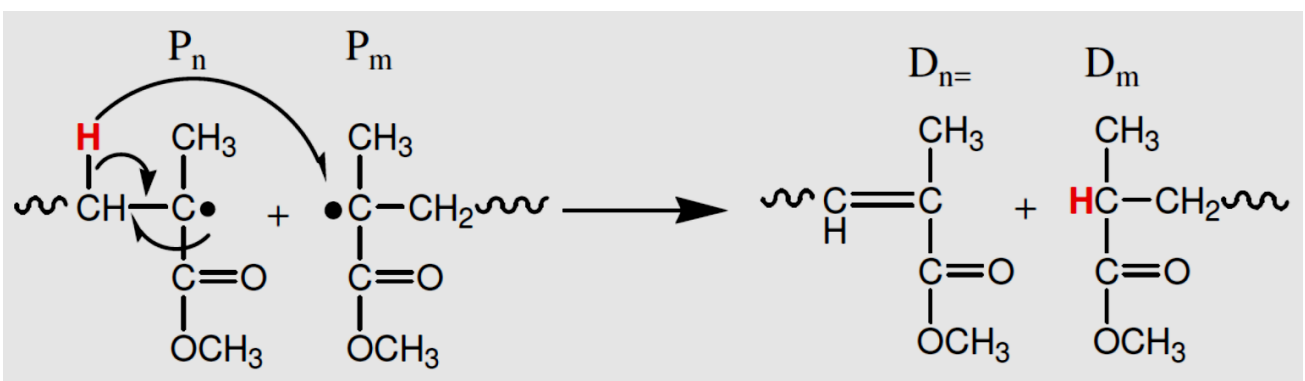
The reaction rate depends on the concentration of the live end groups:



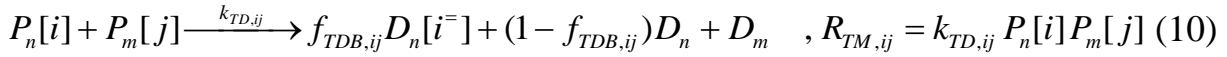
The formation of head-to-head segment dyads can be tracked by including the optional **HTHFLOW** and **HTHFRAC** (head-to-head flow and head-to-head fraction) attributes in the attribute list on the **Polymers**. Head-to-head sequences can contribute to thermal instability and may cause degradation during storage or subsequent processing.

Termination by disproportionation

In disproportionation reactions, the radical at the end of one chain attacks a hydrogen atom at the second-to-last carbon atom in the second chain, forming two dead polymer molecules with no net change in molecular weight. Disproportionation results in one of the dead chains having a saturated end group while the other will have an end-group with a terminal double bond. For example:



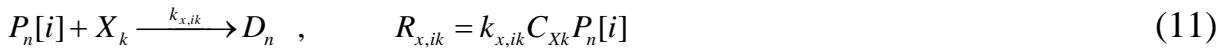
The reaction rate depends on the concentration of the live end groups:



The formation of terminal double bonds can be tracked by including the **TDBFLOW** and **TDBFRAC** (terminal double bond flow and fraction) in the list of attributes on the **Polymers**. Terminal double bonds can contribute to thermal instability and may cause degradation, branching and gelation during storage or subsequent processing.

Inhibition

Inhibition is included as an additional termination mechanism. This involves reaction between a chain radical and a small molecule (inhibitor or impurities) to form a dead chain:



The model assumes that the inhibitor is consumed by the reaction; the polymer mass generation rate is adjusted accordingly.

2.6. Gel effect

Bimolecular termination reactions between chain radicals become diffusion controlled at high polymer concentrations or high conversion leading to an increase in the polymerization rate and molecular weight. This condition is known as the *gel effect* or Trommsdorff effect. At high polymer concentrations, the increased viscosity of the reaction medium imposes a diffusional limitation on the polymer chains, which leads to lower effective termination rates. Typically the termination rate coefficients are affected first by the gel effect because they involve diffusion of two bulky polymer radicals. Eventually at high enough conversions, even the propagation, initiation, chain transfer reactions, and the initiator efficiency are lowered by the gel effect.

Hence, in general it may be necessary to allow gel/glass effects for all the polymerization reactions in the built-in kinetic scheme.

The diffusional limitation is usually modeled by multiplying the low conversion reaction rate coefficients, k_o , by a gel effect factor, GF , that decreases with increasing conversion. Hence the effective rate coefficient for a reaction is given by:

$$k_{eff} = k_o GF \quad (12)$$

Several empirical and semi-empirical correlations relating the gel effect factor to conversion and operating conditions are available in the literature. Currently two of these have been implemented as built-in correlations in Aspen Polymers. Users will be able to use these gel effect correlations simply by specifying the correlation number and the parameters.