School of Engineering
Institute of Materials
Laboratory of Macromolecular
and Organic Materials

Chain-Growth Polymerizations

1. Idealized Chain-Growth Polymerization

In chain-growth polymerizations, an active center is generated by a reaction of an initiator with a first monomer, and then many monomers rapidly add to an active center of a growing chain until that center is deactivated. Prototypical examples of chain growth polymerizations comprise a radical polymerization, certain cationic and anionic polymerizations as well as transition-metal-catalyzed (or "insertion") polymerizations.

- **The first step of a chain-growth polymerization is the initiation reaction, during which the "active center" is formed with the aid of an "initiator". This active center is a reactive intermediate that starts the growth of a polymer chain.** The duration of the initiation process can vary, typically from seconds to minutes, depending on the type of polymerization, the nature of the initiator, and specific reaction conditions such as temperature, solvent, and monomer concentration. Typically, the initiation step has a rate comparable to termination and transfer, and much lower than propagation, so that new chains continue to be initiated throughout the entire time of polymerization. In free radical polymerization, for instance, thermal or photoinitiators generate free radicals that react with monomers to create a radical-based active center, while cationic and anionic polymerizations utilize strong bases or acids, respectively, and transition-metal-catalyzed polymerizations are initiated by the addition of a first monomer to a transition metal center with a "free coordination site" (an empty orbital). The efficiency of the initiation step critically influences the overall rate of polymerization and the properties of the resulting polymer.
- The **propagation reaction** follows initiation and involves the sequential addition of monomer units to the active center of a growing polymer chain. This process occurs rapidly, often on the microseconds to milliseconds time scale, driven by the high reactivity of the active center, allowing for several thousand monomer additions to occur within a few seconds. This process is a "chain reaction" in two senses: *(i)* many monomer addition events can occur after a single initiation event (in the same sense that the term "chain reaction" is also used in radical reaction mechanisms in organic chemistry), and *(ii)* and these reactions occur at the active chain end of a growing polymer chain.
- Finally, a growing chain becomes deactivated in **termination and transfer reactions**, preventing further growth of the deactivated chain, and resulting in a final polymer without an active chain end. One distinguishes **transfer** reactions, where an individual chain is deactivated but a reactive species is generated that can start a new chain (so that the "chain reaction" in the organic chemistry sense continues), from **termination** reactions, where this is not the case (so

that both the individual chain is deactivated and the “chain reaction” ends). As these termination and transfer reactions occur stochastically for each growing polymer chain, they significantly influence the molar mass distribution in chain polymerizations.

In chain-growth polymerizations, consequently, high-molar mass polymers are formed almost immediately after the first initiation, in marked contrast to step-growth polymerizations, where intermediate-sized molecules are prevalent initially. In chain growth polymerizations, there are only monomer, high-molar-mass polymer, and initiator species, and no significant amounts of “intermediate size” molecules. Just the number of polymer molecules in the reaction mixture increases with conversion and reaction time, and in first approximation, no significant changes of the molar mass distribution occur over time.

2. Molar Mass Distribution in Chain-Growth Polymerization

The expected molar mass distribution for an idealized chain growth polymerization can be derived, by initially ignoring the possibility of chain transfer reactions, gel and glass effects, different termination modes, or upstream reactions preceding initiation. In this case, the chain length of the obtained macromolecule is identical to its size prior to the termination.

A chain with x repeat units is formed by a sequence of x–1 propagation steps after initiation (which consumes already one monomer). The cumulated probability to find a chain of x repeat units, $P(x)$, i. e. the probability that x–1 monomer additions have occurred and that the next reaction is a termination, is given by

$$P(x) = p^{x-1}(1-p)\,, \tag{1}$$

where p is the probability of a single propagation step. $1-p$ is accordingly the probability that chain growth gets stopped. p is defined as the ratio of the propagation rate, R_p, to the sum of all relevant rates,

$$p = \frac{R_p}{R_p + R_t}\quad , \tag{2}$$

with R_t being the rate of termination. The initiation rate, R_i, can be ignored in this context, because in a well-designed polymerization, R_i is usually leading quickly to a steady state where a sufficient number of active chains is generated at a constant concentration (see below). Note also that the use of p here is comparable to the use of *conversion* in step-growth polymerization, which can be seen as the probability of any functional group to react and to lead to a propagation event.

Equation 1 is the **number-distribution function** and, in its mathematical form identical to that of a step-growth polymerization. The number of chains containing x repeat units is accordingly given by

$$N_x = NP(x) = Np^{x-1}(1-p)\ , \tag{3}$$

where N is the total number of chains in the system, which is usually equivalent to the number of termination events that have taken place and therefore given by

$$N = N_0(1-p)\,. \tag{4}$$

Here, N_0 is the average number of repeat units per chain, i. e., those monomers that have become part of a polymer chain (not be confused with the total number of initially present monomers). For the **weight-distribution function**, it follows

$$w_x = \frac{m_x}{\sum m_x} = \frac{N_x(x\bar{M}_0)}{N_0\bar{M}_0} = \frac{xN_x}{N_0} = x(1-p)^2 p^{x-1} \ . \tag{5}$$

Hence, the molar mass of an idealized chain-growth polymerization usually follows a Flory-Schulz distribution. Number-average molar mass, weight-average molar mass, and dispersity (Đ = 2) are identical to those of a step growth polymerization.

3. Free Radical Polymerization

3.1 Molar Mass Distribution in Free Radical Polymerization

In general, the description of the molar mass distribution in free radical polymerization is more complex than outlined above because it involves two different termination modes, disproportionation and combination, and it is significantly affected by transfer reactions and additional effects at high conversion, namely the gel and glass effects, where the steady-state assumption is not anymore valid.

In case of termination by disproportionation (transfer of a hydrogen from one active chain to another one), and at sufficiently low conversions in the steady-state regime (see below), the most probable molar mass distribution is a Schulz-Flory distribution, according to the considerations outlined in Equations 1–5.

In case of **termination by combination** (the coupling of two active chains by radical combination of their active chain ends), one needs to consider that two chains of independent lengths y and z are coupled to give a chain of length $x = y + z$, which doubles the average molar mass and also renders the molar mass distribution more narrow (because the probability to produce chains with intermediate z is higher than that of very small or large z). The probabilities of finding chains with lengths y or z, respectively, are given by analogous expressions to Equation 1:

$$P(y) = p^{y-1}(1-p) \qquad \text{and} \qquad P(z) = p^{z-1}(1-p)\,, \tag{6, 7}$$

with the probability of a propagation step, p, being defined as in Equation 2. The cumulative probability of a coupling event taking place between these chains is then given by

$$P(y+z) = P(y)\cdot P(z) = p^{y-1}p^{z-1}(1-p)^2 \ = p^{x-2}(1-p)^2\,. \tag{8}$$

Moreover, because a chain of size x can also be obtained by coupling of chains with (y+1) and (z–1) repeat units, or (y–1) and (z+1) repeat units, or (y+2) and (z–2) repeat units, etc., there are a total of (x–1) possible pathways of producing a chain of length x (if x were an odd number, there would be x pathways but this distinction can be ignored for large chain sizes). Therefore, the cumulative probability of finding a chain with length x must be the sum of probabilities for which all the different combinations of y and z equal x, resulting in the **number-distribution function**

$$P(x) = \sum P(y+z) = (x-1)p^{x-2}(1-p)^2\,. \tag{9}$$

For the total number of polymers, N, a factor $1/2$ needs to be considered to account for the consumption of two growing chains per termination event.

$$N = \frac{N_0(1-p)}{2} . \tag{10}$$

The total number of x-mers is accordingly given by

$$N_x = NP(x) = \frac{N_0(1-p)}{2}(x-1)p^{x-2}(1-p)^2 , \tag{11}$$

and the **weight-distribution function** is accordingly derived as

$$w_x = \frac{m_x}{\sum m_x} = \frac{N_x(x\bar{M}_0)}{N_0\bar{M}_0} = \frac{xN_x}{N_0} = \frac{x}{2}(x-1)p^{x-2}(1-p)^3 . \tag{12}$$

The number-average degree of polymerization, $\bar{X}_n$, in this case is (with the help of Equation 10):

$$\bar{X}_n = \frac{N_0}{N} = \frac{2}{1-p} . \tag{13}$$

The weight-average degree of polymerization, $\bar{X}_w$, is more complicated to derive and we provide here just the solution:

$$\bar{X}_w = \frac{2+p}{1-p} . \tag{14}$$

The **dispersity** is hence defined as

$$Đ = \frac{\bar{X}_w}{\bar{X}_n} = \frac{(2+p)(1-p)}{2(1-p)} = \frac{2+p}{2} \tag{15}$$

and approaches Đ =1.5 for p tending to unity, i. e., for high molar mass polymers. Thus, termination by combination results indeed in a narrower molar mass distribution compared to disproportionation.

For commercial polymer grades, however, the dispersity is often much larger, due to side reactions, branching, or different active centers in the case of heterogeneous catalysis. The average molar masses obtained in chain-growth reactions are generally much higher than in step-growth polymerizations and may even reach values of several millions g/mol.

Note that, in all of the above derivations, p has been defined as a relative probability of a propagation step (the probability that a monomer addition will occur), i. e., as the rate of propagation divided by the sum of rates of all reactions that a propagating radical may undergo (in this reader, we considered propagation and termination). While this use of p is conceptually comparable to the conversion p in step growth polymerizations (as both represent probabilities related to reactions), they differ in their specific definitions. Furthermore, the above equations apply only to the polymer fraction of the reaction mixture, while the equations derived for step-growth polymerizations apply to the entire reaction mixture.

3.2 Steady-State Kinetics of Free Radical Polymerization

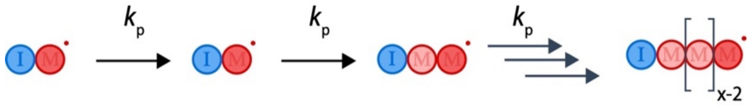
In industrial processes involving free radical polymerization, the polymerization conditions (initiator chemistry, temperature, concentration) are chosen such that the radical concentration converges (rapidly) to a constant **steady-state value** because the initiation and termination rates are equal. This is demanded by process engineering because, the polymerization would stop if the termination rate was too high, and the reaction would "run away" (the reactor may go out of control) if the initiation rate was too high.

Finding a kinetic expression for the rate of polymerization starts with the **rate of initiation**, R_i. In free radical polymerization, the initiation of chain-growth is preceded by a slow and therefore rate-determining step during which the initiator radical is formed. R_i therefore does not exhibit first-order kinetics in relation to the monomer but quasi-zeroth order. This means that the rate of initiation remains constant over a certain range of monomer concentrations:

$$R_i = \frac{\mathrm{d}[\mathrm{I}^\cdot]}{\mathrm{d}t} = 2fk_i[\mathrm{I}]\,, \tag{16}$$

with the initiator efficiency $f \leq 1$ that represents the fraction of initiator radicals that successfully start the chain growth (but that is limited by side reactions, e. g., immediate recombination), and k_i the rate for the initiator decomposition. The factor 2 in Equation 16 is introduced by convention because a typical (spin-paired) initiator decomposes into two initiator radicals.

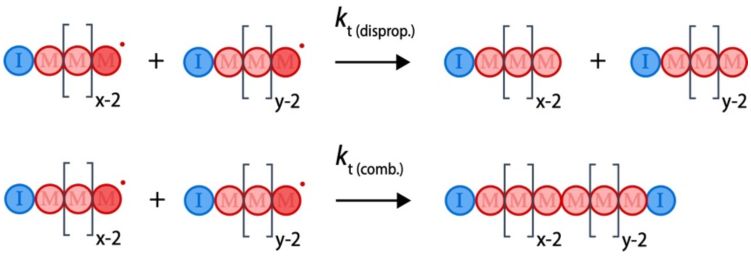
For simplification, one assumes the rate constants of propagation and termination, k_p and k_t, respectively, to be independent of the molar mass of the growing chain (all active centers are assumed to have the same reactivity). Any addition of monomer, regardless of the size of the growing chain, is then characterized by the same k_p value, which is a reasonable assumption, given that every growing chain's radical is predominantly surrounded by monomer molecules in the reaction mixture, making rapid bimolecular collision inevitable. Provided that the propagation rate is much faster than the initiation rate, the **rate of polymerization** is equivalent to the rate of monomer disappearance and can accordingly be expressed as the *propagation* rate, R_p, :



$$\frac{-\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = R_p = k_p[\mathrm{M}^\cdot][\mathrm{M}]\,, \tag{17}$$

where [M] is the monomer concentration and $[\mathrm{M}^\cdot]$ is the total concentration of all radicals of size $\mathrm{M}_1^\cdot$ and larger.

Termination is the disappearance of radicals, which is a bimolecular process involving two radicals and hence second order in radical concentration (proportional to the square of radical concentration), with a factor 2 accounting for two radicals being consumed in every termination reaction and k_t comprising both rate constants for *combination* and *disproportionation* :



$$\frac{-\mathrm{d}[\mathrm{M}^{\cdot}]}{\mathrm{d}t} = R_t = 2k_t[\mathrm{M}^{\cdot}]^2\,. \tag{18}$$

Assuming **steady-state kinetics**, i. e., demanding the initiation and termination rates to be equal, this allows the (unknown) radical concentration to be expressed in terms of the rate constants of initiation and termination as well as the initiator concentration :

$$R_i = R_t = 2k_t[\mathrm{M}^{\cdot}]^2 = 2fk_i[\mathrm{I}]\,. \tag{19}$$

Resolving for $[\mathrm{M}^{\cdot}]$ results in

$$[\mathrm{M}^{\cdot}] = \sqrt{\frac{fk_i[\mathrm{I}]}{k_t}}\,. \tag{20}$$

Combining Equations 17 and 20 gives an expression for the propagation rate, R_p, which is equivalent to the rate of the overall polymerization, provided that propagation is much faster than the initiation, which is usually the case in radical polymerizations:

$$R_p = k_p\sqrt{\frac{fk_i[\mathrm{I}]}{k_t}}\,[\mathrm{M}]\,. \tag{21}$$

Hence, a stable free radical polymerization process shows a reaction order of 0.5 with respect to the initiator concentration. The square-root dependence of the rate of polymerization on initiator concentration ("square-root law") arises because the rates of initiation and termination are equal in steady-state conditions, and termination is a bimolecular process, while initiation is first order in initiator concentration. For example, **doubling the initiator concentration, and thus the rate of initiation, results in only a $\sqrt{2}$-fold increase in the polymerization rate.**

3.3 Kinetic Chain Length

The ratio of the propagation to the initiation rate gives an expression for the **kinetic chain length**, $\bar{\nu}$, a theoretical polymer chain length, which is **defined as the average number of monomer molecules consumed per each radical that has initiated a polymer chain**. The kinetic chain length is distinguished from the degree of polymerization (the number of monomers in the final macromolecule) because the latter is affected by a variety of additional factors (mode of termination, gel and/or glass effect, chain transfer reactions). The average number of monomer molecules consumed by each radical is equal to the ratio of the rates of propagation and initiation; and the latter is, in steady-state conditions, chosen to be equal to the rate of termination, so that it follows from Equations 2–6 that

$$\bar{\nu} = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p[\mathrm{M}^\cdot][\mathrm{M}]}{2k_t[\mathrm{M}^\cdot]^2} = \frac{k_p[\mathrm{M}]}{2k_t[\mathrm{M}^\cdot]} = \frac{k_p[\mathrm{M}]}{2k_t\sqrt{\frac{fk_i[\mathrm{I}]}{k_t}}} = \frac{{k_p}^2[\mathrm{M}]^2}{2k_tR_p}. \tag{22}$$

Combining Equations 21 and 22 leads to an expression for the dependence of the kinetic chain length on both monomer and initiator concentration:

$$\bar{\nu} = \frac{k_p[\mathrm{M}]}{2\sqrt{k_tfk_i[\mathrm{I}]}}. \tag{23}$$

Equations 22 and 23 imply that the **kinetic chain length $\bar{\nu}$ is inversely proportional to the rate of polymerization and the radical concentration**, which is of great practical significance. Thus, any increase in R_p (for example by increasing the reaction temperature or by increasing the radical concentration) leads to a corresponding decrease in kinetic chain length. Likewise, an increased initiator concentration leads to an increased polymerization rate (Equation 19) but a decrease of the kinetic chain length.

The kinetic chain length relates to number-average degree of polymerization, $\bar{X}_n$, but depends on the mode of termination. In case of disproportionation, both quantities are identical ($\bar{X}_n = \bar{\nu}$), whereas for termination by combination, $\bar{X}_n = 2\bar{\nu}$ (valid only for the low conversion regime, when no gel and glass effects play a role, and only in case of the absence of chain transfer events).