Living and Controlled Polymerizations

1. Introduction

"Living" and "controlled" chain growth polymerizations (like regular chain growth polymerizations) start with the initiation of a polymer chain with an active chain end and propagation but (unlike regular chain growth polymerizations), there are no termination or transfer reactions because they are either chemically impossible (in "living" polymerizations) or at least strongly kinetically suppressed (in "controlled" polymerizations). In both cases, *(i)* steady-state conditions hence do not apply. Moreover, *(ii)* initiation is typically considered to be fast compared to propagation. Therefore, the boundary conditions for the derivation of the polymerization kinetics are entirely different from regular chain growth processes.

An important consequence is that propagation only stops when there is no more monomer left. Even then, the chain ends remain active ("living"), so that the polymerization can be restarted at any time by adding more (or a different) monomer as until they are "quenched", i. e., terminated on purpose by adding a quenching reagent that may also serve to introduce a chemical functional end group.

The prototypical example of a living polymerization is the **anionic polymerization** of vinyl monomers. Typical initiators are lithium organyls (carbanions with lithium counterions) that are very strong nucleophiles and attack the C=C bond of vinyl monomers to generate a carbanionic chain end. Typical monomers are vinyl monomers with electron-withdrawing substituents because these stabilize the carbanionic chain ends. Anionic polymerizations are quenched with electrophiles, in the simplest case with a proton from water or methanol added as a quenching agent. Therefore, strictly anhydrous conditions and the absence of other protic solvents and electrophiles (like carbon dioxide) must be ensured to avoid premature quenching, the polymerization is carried out under inert gas atmosphere, and monomer as well as solvents must be well dried beforehand.

2. Kinetics of Living Polymerization

Since the initiation with lithium organyls is fast compared to the propagation, all chains approximately begin to grow at the same time. Assuming that all chains grow with the same rate of propagation, R_p, we can generalize for the consumption of monomer over time:

$$R_p = -\frac{\mathrm{d[M]}}{\mathrm{d}t} = k_p[\mathrm{P}^{\ominus}][\mathrm{M}] = k_p[\mathrm{I}]_0[\mathrm{M}] \qquad (1)$$

where $[\mathrm{P}^{\ominus}]$ is the concentration of all active chain ends, whose amount is equivalent to the initial initiator concentration $[\mathrm{I}]_0$ if initiation is complete and effectively instantaneous compared to the propagation. The rate law in Equation 1 is a linear, first-order differential equation for [M], which can be analytically solved by integration, resulting in the time-dependent monomer concentration function

$$[\mathrm{M}] = [\mathrm{M}]_0 e^{-k_p [\mathrm{I}]_0 t}\,, \tag{2}$$

with $[\mathrm{M}]_0$ being the initial monomer concentration. **The monomer concentration hence decreases exponentially with time.**

We use again the kinetic chain length, $\bar{\nu}$, which is given by the ratio of monomers consumed until time t and the total number of polymer chains (which, in turn, is equal the initial initiator concentration)

$$\bar{\nu} = \frac{[\mathrm{M}]_0 - [\mathrm{M}]}{[\mathrm{I}]_0} = \frac{p[\mathrm{M}]_0}{[\mathrm{I}]_0}\,, \tag{3}$$

with $p = ([\mathrm{M}]_0 - [\mathrm{M}])/[\mathrm{M}]_0$ being the conversion of monomers. Note that by definition, $\bar{\nu} = 0$ at the beginning of the reaction (when $[\mathrm{M}] = [\mathrm{M}]_0$), while the degree of polymerization equals 1 (as the initiated species contains already one repeat unit). **It follows that the initial ratio of monomer-to-initiator concentration is therefore an important control parameter for the molecular weight of the final polymer.**

3. Molecular Weight Distribution and Dispersity

In order to find an expression for the distribution of chain lengths, one may write explicit equations for the rate of the consumption of any chain length, starting with a polymer with degree of polymerization of 1 ($\mathrm{P}_1^{\ominus}$, which is the initiated species), then for the next higher chain length (corresponding to $\mathrm{P}_2^{\ominus}$), and so on. Generalization of this procedure will lead us to a **Poisson distribution** for the molecular weight.

For this purpose, it will be helpful to differentiate the kinetic chain length with respect to time, using the expression for $\mathrm{dM}/\mathrm{d}t$ in Equation 1.

$$\frac{\mathrm{d}\bar{\nu}}{\mathrm{d}t} = -\frac{1}{[\mathrm{I}]_0}\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_p[\mathrm{M}]\,. \tag{4}$$

The consumption of $\mathrm{P}_1^{\ominus}$ is simply given by the rate of the first propagation step

$$-\frac{\mathrm{d}[\mathrm{P}_1^{\ominus}]}{\mathrm{d}t} = k_p[\mathrm{P}_1^{\ominus}][\mathrm{M}]\,. \tag{5}$$

Application of the *chain rule* known from calculus ("chain" in this context has nothing to do with a polymer!) and insertion of the result of Equation 4 lead to

$$\frac{\mathrm{d}[\mathrm{P}_1^{\ominus}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{P}_1^{\ominus}]}{\mathrm{d}\bar{\nu}} \frac{\mathrm{d}\bar{\nu}}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{P}_1^{\ominus}]}{\mathrm{d}\bar{\nu}} k_p[\mathrm{M}] \,. \tag{6}$$

By comparing the right-hand-sides of Equations 5 and 6, it follows for the differential of $[\mathrm{P}_1^{\ominus}]$ with respect to the kinetic chain length:

$$-\frac{\mathrm{d}[\mathrm{P}_1^{\ominus}]}{\mathrm{d}\bar{\nu}} = [\mathrm{P}_1^{\ominus}] \,, \tag{7}$$

which can be solved for the concentration of $\mathrm{P}_1^{\ominus}$:

$$[\mathrm{P}_1^{\ominus}] = [\mathrm{P}_1^{\ominus}]_0 e^{-\bar{\nu}} = [\mathrm{I}]_0 e^{-\bar{\nu}} \,. \tag{8}$$

Hence, $\mathrm{P}_1^{\ominus}$ is the exclusive species at the beginning of the polymerization (due to the instantaneous initiation; $\bar{\nu}$ equals zero in this case) and its concentration decreases exponentially with increasing kinetic chain length.

This exercise can be repeated for the next larger species, $\mathrm{P}_2^{\ominus}$, in which case the rate expression for its concentration change over time is a bit more complex because it is formed from $\mathrm{P}_1^{\ominus}$ and consumed to form $\mathrm{P}_3^{\ominus}$ at any moment. The rate of the change in $[\mathrm{P}_2^{\ominus}]$ over time is therefore

$$\frac{\mathrm{d}[\mathrm{P}_2^{\ominus}]}{\mathrm{d}t} = k_p[\mathrm{P}_1^{\ominus}][\mathrm{M}] - k_p[\mathrm{P}_2^{\ominus}][\mathrm{M}] = \frac{\mathrm{d}\bar{\nu}}{\mathrm{d}t}\left([\mathrm{P}_1^{\ominus}] - [\mathrm{P}_2^{\ominus}]\right) , \tag{9}$$

where we used Equation 4 to establish the right-hand-side. Application of the *chain rule* and solving for $[\mathrm{P}_2^{\ominus}]$ yields

$$[\mathrm{P}_2^{\ominus}] = \bar{\nu}[\mathrm{I}]_0 e^{-\bar{\nu}} \,, \tag{10}$$

Following the same procedure for $[\mathrm{P}_3^{\ominus}]$, results in

$$[\mathrm{P}_3^{\ominus}] = \frac{1}{2}\bar{\nu}^2[\mathrm{I}]_0 e^{-\bar{\nu}} \,. \tag{11}$$

This approach can be expressed by a generalized form for any x-mer

$$[\mathrm{P}_x^{\ominus}] = \frac{1}{(x-1)!}\bar{\nu}^{x-1}[\mathrm{I}]_0 e^{-\bar{\nu}} \,. \tag{12}$$

The number fraction of x-mers is then given by the ratio of their own concentration to the total concentration of all chains (equal to the initiator concentration), and results in a **Poisson distribution**:

$$P_x = \frac{[\mathrm{P}_x^{\ominus}]}{[\mathrm{I}]_0} = \frac{\bar{\nu}^{x-1}e^{-\bar{\nu}}}{(x-1)!} \tag{13}$$

The Poisson distribution is a very narrow distribution compared to those obtained by step-growth or regular chain-growth polymerizations. Note that the width of this distribution, although narrow, increases with increasing degree of polymerization. However, its relative width normalized by $\bar{v}$ decreases steadily. **Prerequisites for obtaining this narrow distribution are the equal reactivity of chain ends towards monomer throughout the entire polymerization, the vry rapid initiation compared to propagation (so that all chains approximately start to grow at the same time and grow at the same rate), moreover an irreversible propagation (depolymerization should be negligible), and the absence of statistical termination events.**

The number average degree of polymerization, $\bar{X}_n$, can accordingly be calculated from the Poisson distribution by considering the probability to find each x-mer.

$$\bar{X}_n = \sum_x x\,P_x = \sum_x x\frac{\bar{v}^{x-1}e^{-\bar{v}}}{(x-1)!} = e^{-\bar{v}}\sum_x \frac{x\bar{v}^{x-1}}{(x-1)!} = e^{-\bar{v}}\frac{\mathrm{d}}{\mathrm{d}\bar{v}}\sum_x \frac{\bar{v}^x}{(x-1)!} \tag{14}$$

Here, we rearranged the left-hand-side of Equation 21 by recognizing that the exponential term does not depend on x and can therefore be factored out of the sum. Moreover, $x\bar{v}^{x-1}$ can be written as $\mathrm{d}(\bar{v}^x)/\mathrm{d}\bar{v}$. To get rid of the factorials, we use the infinite series expansion of $e^{\bar{v}}$ (see Equation 19 in the Appendix) and differentiate the resulting product according to the *product rule* for differentiation:

$$\bar{X}_n = e^{-\bar{v}}\frac{\mathrm{d}}{\mathrm{d}\bar{v}}\sum_x \bar{v}\frac{\bar{v}^{x-1}}{(x-1)!} = e^{-\bar{v}}\frac{\mathrm{d}}{\mathrm{d}\bar{v}}(\bar{v}e^{\bar{v}}) = e^{-\bar{v}}(\bar{v}e^{\bar{v}} + e^{\bar{v}}) = 1 + \bar{v} \approx \frac{p[\mathrm{M}]_0}{[\mathrm{I}]_0} \tag{15}$$

For sufficiently large degrees of polymerization, it follows that the number-average degree of polymerization of the final polymer, $\bar{X}_n = \bar{v} + 1 \approx \bar{v}$. Once the polymerization is complete and has been quenched, the resulting number average molar mass is equal to $[\mathrm{M}]_0/[\mathrm{I}]_0$, i. e., the mass of reacted monomers to the concentration of living chain ends.

A similar approach leads to an expression for $\bar{X}_w$ as well, starting from its definition

$$\bar{X}_w = \sum_x x\,w_x = \frac{\sum_x x^2 P_x}{\sum_x x\,P_x} = \frac{\sum_x x^2 \frac{\bar{v}^{x-1}e^{-\bar{v}}}{(x-1)!}}{\bar{X}_n} = \frac{\sum_x x^2 \frac{\bar{v}^{x-1}e^{-\bar{v}}}{(x-1)!}}{1+\bar{v}}, \tag{16}$$

where w_x and P_x (Equation 13) are the weight distribution and number distribution function, respectively. Moreover, we used here the just established result for $\bar{X}_n$ according to Equation 15. For resolving the numerator of Equation 16, see Equation 20 and 21 in the Appendix. We obtain

$$\bar{X}_w = \frac{1 + 3\bar{v} + \bar{v}^2}{1+\bar{v}}. \tag{17}$$

The dispersity for sufficiently large $\bar{v}$ can therefore be approximated as

$$Đ = \frac{\bar{X}_w}{\bar{X}_n} = \frac{1 + 3\bar{v} + \bar{v}^2}{(1 + \bar{v})^2} = \frac{(1 + \bar{v})^2 + \bar{v}}{(1 + \bar{v})^2} = 1 + \frac{\bar{v}}{(1 + \bar{v})^2} \approx 1 + \frac{1}{\bar{v}}. \qquad (18)$$

The dispersity of a polymer prepared by living chain growth polymerization will hence be close to 1. Other controlled polymerization methods exist as well to produce **"monodisperse" polymers**. As long as the initiation is rapid compared to propagation, the individual propagation steps are irreversible, and the absence of a statistical termination event is ensured, the above considerations apply.

Appendix:

$$e^{y} = \sum_{x} \frac{y^{x}}{x!} = \sum_{x} \frac{y^{x-1}}{(x-1)!} \tag{19}$$

For simplifying the numerator in Equation 16, we use $x\bar{v}^{x-1} = \mathrm{d}(\bar{v}^{x})/\mathrm{d}\bar{v}$ until Equation 19 can be applied in the last step:

$$\begin{aligned}
\sum_{x} x^{2} \frac{\bar{v}^{x-1} e^{-\bar{v}}}{(x-1)!} &= e^{-\bar{v}} \sum_{x} x^{2} \frac{\bar{v}^{x-1}}{(x-1)!} = e^{-\bar{v}} \sum_{x} x \frac{x\bar{v}^{x-1}}{(x-1)!} = e^{-\bar{v}} \frac{\mathrm{d}}{\mathrm{d}\bar{v}} \sum_{x} x \frac{\bar{v}^{x}}{(x-1)!} \\
&= e^{-\bar{v}} \frac{\mathrm{d}}{\mathrm{d}\bar{v}} \bar{v} \sum_{x} \frac{x\bar{v}^{x-1}}{(x-1)!} = e^{-\bar{v}} \frac{\mathrm{d}}{\mathrm{d}\bar{v}} \bar{v} \frac{\mathrm{d}}{\mathrm{d}\bar{v}} \sum_{x} \frac{\bar{v}^{x}}{(x-1)!} \\
&= e^{-\bar{v}} \frac{\mathrm{d}}{\mathrm{d}\bar{v}} \bar{v} \frac{\mathrm{d}}{\mathrm{d}\bar{v}} \bar{v} \sum_{x} \frac{\bar{v}^{x-1}}{(x-1)!} = e^{-\bar{v}} \frac{\mathrm{d}}{\mathrm{d}\bar{v}} \bar{v} \frac{\mathrm{d}}{\mathrm{d}\bar{v}} \bar{v} e^{\bar{v}}
\end{aligned} \tag{20}$$

It remains to solve the derivates of the right-hand-side of Equation 20 according to the *product rule* (known from calculus):

$$\begin{aligned}
e^{-\bar{v}} \frac{\mathrm{d}}{\mathrm{d}\bar{v}} \bar{v} \frac{\mathrm{d}}{\mathrm{d}\bar{v}} \{\bar{v}e^{\bar{v}}\} &= e^{-\bar{v}} \frac{\mathrm{d}}{\mathrm{d}\bar{v}} \bar{v} \{e^{\bar{v}} + \bar{v}e^{\bar{v}}\} = e^{-\bar{v}} \frac{\mathrm{d}}{\mathrm{d}\bar{v}} \{\bar{v}e^{\bar{v}} + \bar{v}^{2}e^{\bar{v}}\} \\
&= e^{-\bar{v}} \{e^{\bar{v}} + \bar{v}e^{\bar{v}} + 2\bar{v}e^{\bar{v}} + \bar{v}^{2}e^{\bar{v}}\} = 1 + 3\bar{v} + \bar{v}^{2}
\end{aligned} \tag{21}$$