Analytical model and Monte Carlo simulations of polymer degradation with improved chain cut statistics

Supplementary Material

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1 Degradation curve for $N_P > 2l+1$

1.1 Number of chain ends

The degradation of polymers by hydrolysis is a process in which a water molecule cuts a bond of a polymer chain. A random cut mechanism of a linear chain is considered. In this case, the probability of a chain cut is equal for every bond of the chain. If small fragments are generated by cuts near the end of the chain, they can diffuse away and lead to a mass loss. If the fragments are too big to diffuse, still the average degree of polymerization is reduced. The maximum size of diffusing fragments l depends on the hydrolicity of the monomers. The probability of a chain cut is proportional to the number of breakable bonds N_{bond}. A mixture with N_{chain} chains and a degree of polymerization N_P, which is the average number of repeating units per chain, contains $N_{\mathrm{chain}}(N_P-1)$ breakable bonds which connect the individual repeating units. The degree of polymerization can be expressed by the number of repeating units RU and the number of chain ends NE: $N_P = RU/(NE/2)$. The number of breakable bonds per chain cut is therefore $N_{\mathrm{bond}} = RU - NE/2$. The reaction rate v_{reac} of chain cuts is

$$v_{\mathrm{reac}} = kN_{\mathrm{bond}} \tag{1}$$

Here, k is the reaction constant. Every chain cut, which does not create a diffusible fragment, creates two additional end groups. A diffusible fragment can be created by a chain cut on both sides of a chain. The probability P_{diff} to create a diffusible fragment in one chain cut is

$$P_{\mathrm{diff}} = 2\frac{l}{N_P-1} \tag{2}$$

This means that the change in the number of end groups for a chain cut is

$$\begin{aligned}
\frac{\mathrm{dNE}}{\mathrm{d}t} &= k\left(\mathrm{RU} - \frac{\mathrm{NE}}{2}\right)P_{\mathrm{inner}}\left(2 - 4\frac{\mathbf{l}}{N_P-1}\right)\\
&= kP_{\mathrm{inner}}\left(2\mathrm{RU} - \mathrm{NE} - \frac{4\mathrm{RU}l}{N_P-1} + \frac{2\mathrm{NE}l}{N_P-1}\right)\\
&= kP_{\mathrm{inner}}\left(2\mathrm{RU} - \mathrm{NE} - \frac{4l}{N_P-1}\frac{\mathrm{NE}}{2}\left(N_P-1\right)\right)\\
&= kP_{\mathrm{inner}}\left(2\mathrm{RU} - \mathrm{NE} - 2\mathrm{NE}l\right)
\end{aligned} \tag{3}$$

Here, P_{inner} is the relative reactivity of an inner bond in comparison to the reactivity of a bond at the chain end. The number of repeating units in the polymer, which is proportional to the average degree of polymerization, only decreases if a diffusible fragment is created. The average number of repeating units of a diffusible fragment is $\frac{1}{2}(l+1)$. As a result, the number of repeating units in the system decreases via

$$\begin{aligned}
\frac{\mathrm{dRU}}{\mathrm{d}t} &= -k\left(\mathrm{RU} - \frac{\mathrm{NE}}{2}\right)\frac{2l}{N_P-1}\frac{1}{2}\left(l+1\right)\\
&= -\frac{k\mathrm{NE}}{2}l\left(l+1\right)
\end{aligned} \tag{4}$$

The second derivative of NE is

$$\begin{aligned}
\frac{\mathrm{d}^2\mathrm{NE}}{\mathrm{d}t^2} &= kP_{\text{inner}}\left(2\frac{\mathrm{dRU}}{\mathrm{d}t} - \frac{\mathrm{dNE}}{\mathrm{d}t} - 2l\frac{\mathrm{dNE}}{\mathrm{d}t}\right) \\
&= kP_{\text{inner}}\left(-k\mathrm{NE}l\,(l+1) - \frac{\mathrm{dNE}}{\mathrm{d}t} - 2l\frac{\mathrm{dNE}}{\mathrm{d}t}\right) \\
&= kP_{\text{inner}}\left(\frac{\mathrm{dNE}}{\mathrm{d}t}\,(-2l-1) - k\mathrm{NE}l\,(l+1)\right) \qquad (5)
\end{aligned}$$

Here, it is assumed that the length of a diffusible fragment l does not change during the process of degradation.
With the exponential approach

$$\mathrm{NE}(t) = ce^{at},$$

equation 5 converts to

$$ca^2 = kP_{\text{inner}}\left(ca\,(-2l-1) - ckl\,(l+1)\right)$$

This quadratic equation is solved:

$$\begin{aligned}
a^2 - kP_{\text{inner}}\left(a\,(-2l-1) - kl\,(l+1)\right) &= 0 \\
a^2 + kP_{\text{inner}}a\,(2l+1) + k^2P^2P_{\text{inner}}l\,(l+1) &= 0
\end{aligned}$$

$$\begin{aligned}
a &= -\frac{kP_{\text{inner}}}{2}\,(2l+1) \pm \sqrt{\frac{k^2P_{\text{inner}}^2}{4}\,(2l+1)^2 - k^2P^2P_{\text{inner}}l\,(l+1)} \\
&= -\frac{kP_{\text{inner}}}{2}\,(2l+1) \pm \frac{k}{2}\sqrt{P_{\text{inner}}^2(2l+1)^2 - 4P_{\text{inner}}l(l+1)}
\end{aligned}$$

The choice of P_{inner} determines if the root is positive or negative. The root is 0 for P_{inner}=0 or $P_{\text{inner}}=(4l^2+4l)/(4l^2+4l+1)$. Because 0< P_{inner} <1, we only consider the two cases $P_{\text{inner}} < (4l^2+4l)/(4l^2+4l+1)$ and $P_{\text{inner}} \geq (4l^2+4l)/(4l^2+4l+1)$
We set

$$\begin{cases}
x = i\sqrt{-(P_{\text{inner}}^2(2l+1)^2 - 4P_{\text{inner}}l(l+1))} = i\beta & P_{\text{inner}} < \frac{4l^2+4l}{4l^2+4l+1} \\
x = \sqrt{P_{\text{inner}}^2(2l+1)^2 - 4P_{\text{inner}}l(l+1)} & P_{\text{inner}} \geq \frac{4l^2+4l}{4l^2+4l+1}
\end{cases}$$

Note, that β is a real number and that x=1 for P_{inner}=1. Using a linear combination of both solutions, we get

$$\mathrm{NE}(t) = e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(c_1e^{\frac{kP}{2}xt} + c_2e^{-\frac{k}{2}xt}\right),$$

At t=0, we get

$$c_2 = \mathrm{NE}(0) - c_1$$

and for the derivative (see equation 3)

$$\begin{aligned}
\frac{\mathrm{dNE}}{\mathrm{d}t}(0) &= kP_{\text{inner}}\left(2\mathrm{RU}(0) - \mathrm{NE}(0)\,(1+2l)\right) \qquad (6) \\
&= -kP_{\text{inner}}\frac{1}{2}\,(2l+1)\left(c_1 + (NE(0) - c_1)\right) + c_1\frac{k}{2}x - (NE(0) - c_1)\,\frac{k}{2}x \\
&= \frac{k}{2}\left(-P_{\text{inner}}\,(2l+1)\,NE(0) + 2c_1x - NE(0)x\right) \qquad (7)
\end{aligned}$$

First, we solve the equation for $P_{\text{inner}} \geq (4l^2+4l)/(4l^2+4l+1)$. Comparing Eqs. 6 and 7 delivers

$$c_1 = 2\frac{P_{\text{inner}}}{x}\text{RU}(0) - \frac{1}{2}\left((2l+1)\frac{P_{\text{inner}}}{x} - 1\right)\text{NE}(0) = A + B \tag{8}$$

$$c_2 = -\left(2\frac{P_{\text{inner}}}{x}\text{RU}(0) - \frac{1}{2}\left((2l+1)\frac{P_{\text{inner}}}{x} + 1\right)\text{NE}(0)\right) = -A + B \tag{9}$$

with $A = 2\frac{P_{\text{inner}}}{x}\text{RU}(0) - \frac{1}{2}(2l+1)\frac{P_{\text{inner}}}{x}\text{NE}(0)$ and $B = \frac{NE(0)}{2}$ and therefore

$$\begin{aligned}
\text{NE}(t) = e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t} & \left(2\frac{P_{\text{inner}}}{x}\text{RU}(0) - \frac{1}{2}(2l+1)\frac{P_{\text{inner}}}{x}\text{NE}(0) + \frac{NE(0)}{2}\right)e^{\frac{k}{2}xt} \\
& - \left(2\frac{P_{\text{inner}}}{x}\text{RU}(0) - \frac{1}{2}(2l+1)\frac{P_{\text{inner}}}{x}\text{NE}(0) - \frac{NE(0)}{2}\right)e^{-\frac{k}{2}xt} \\
= e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t} & \left((A+B)\,e^{-\frac{k}{2}xt} + (-A+B)\,e^{-\frac{k}{2}xt}\right) \\
= 2e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t} & \left(A\sinh(\frac{k}{2}xt) + B\cosh(\frac{k}{2}xt)\right) \\
= 2e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t} & \left(\left(2\text{RU}(0) - \frac{1}{2}(2l+1)\,\text{NE}(0)\right)\frac{P_{\text{inner}}}{x}\sinh(\frac{k}{2}xt) + \frac{NE(0)}{2}\cosh(\frac{k}{2}xt)\right)
\end{aligned} \tag{10}$$

$$\frac{\text{NE}(t)}{\text{NE}(0)} = 2e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(\left(2\frac{\text{RU}(0)}{\text{NE}(0)} - \frac{1}{2}(2l+1)\right)\frac{P_{\text{inner}}}{x}\sinh(\frac{k}{2}xt) + \frac{1}{2}\cosh(\frac{k}{2}xt)\right)$$

If $RU(0) \gg \frac{1}{4}(2l+1)\,\text{NE}(0) > NE(0)$, then

$$\text{NE}(t) \approx 2e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(2RU(0)\frac{P_{\text{inner}}}{x}\sinh(\frac{k}{2}xt) + \frac{NE(0)}{2}\cosh(\frac{k}{2}xt)\right) \tag{11}$$

We introduce the critical time

$$t_c = \frac{2}{kx}\,\text{arcCoth}\left(\left(2l+1-4\frac{RU(0)}{NE(0)}\right)\frac{P_{\text{inner}}}{x}\right)$$

For large times $t \gg t_c$, eq. 10 reduces to

$$\text{NE}(t) = 2e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(2\text{RU}(0) - \frac{1}{2}(2l+1)\,\text{NE}(0)\right)\frac{P_{\text{inner}}}{x}\sinh(\frac{k}{2}xt) \tag{12}$$

The derivative of $NE(t)$ is

$$\begin{aligned}
\frac{\text{dNE}}{\text{d}t} =& -kP_{\text{inner}}(2l+1)\,e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(\left(2\text{RU}(0) - \frac{1}{2}(2l+1)\,\text{NE}(0)\right)\frac{P_{\text{inner}}}{x}\sinh(\frac{k}{2}xt) + \frac{NE(0)}{2}\cosh(\frac{k}{2}xt)\right) \\
& + 2e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(\left(2\text{RU}(0) - \frac{1}{2}(2l+1)\,\text{NE}(0)\right)\frac{P_{\text{inner}}}{x}\frac{k}{2}x\cosh(\frac{k}{2}xt) + \frac{NE(0)}{2}\frac{k}{2}x\sinh(\frac{k}{2}xt)\right) \\
=& ke^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(\left(\left(\frac{1}{2}(2l+1)^2\frac{P_{\text{inner}}^2}{x} + \frac{1}{2}x\right)NE(0) - 2(2l+1)\frac{P_{\text{inner}}^2}{x}RU(0)\right)\sinh(\frac{k}{2}xt)\right. \\
& \left. + \left(-(2l+1)\,NE(0) + 2RU(0)\right)P_{\text{inner}}\cosh(\frac{k}{2}xt)\right)
\end{aligned} \tag{13}$$

The function NE(t) has an extreme point at

$$t_1 = \frac{2}{kx}\tanh^{-1}\left(\frac{((2l+1)\,NE(0)-2RU(0))P_{\text{inner}}}{\left(\frac{1}{2}(2l+1)^2\frac{P_{\text{inner}}^2}{x}+\frac{1}{2}x\right)NE(0)-2\,(2l+1)\,\frac{P_{\text{inner}}^2}{x}RU(0)}\right).$$

Now, we solve the equation for $P_{\text{inner}} < (4l^2+4l)/(4l^2+4l+1)$.
With $A = 2\frac{P_{\text{inner}}}{i\beta}\text{RU}(0) - \frac{1}{2}\,(2l+1)\,\frac{P_{\text{inner}}}{i\beta}\text{NE}(0)$ and $B = \frac{NE(0)}{2}$ we get

$$\begin{aligned}
\text{NE}(t) &= e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\quad\left((A+B)\,e^{i\frac{k}{2}\beta t} + (-A+B)\,e^{-i\frac{k}{2}\beta t}\right)\\
&= 2e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(iA\sin(\frac{k}{2}\beta t) + B\cos(\frac{k}{2}\beta t)\right)\\
&= 2e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(\left(2\text{RU}(0) - \frac{1}{2}\,(2l+1)\,\text{NE}(0)\right)\frac{P_{\text{inner}}}{\beta}\sin(\frac{k}{2}\beta t) + \frac{NE(0)}{2}\cos(\frac{k}{2}\beta t)\right)
\end{aligned} \tag{14}$$

$$\frac{\text{NE}(t)}{\text{NE}(0)} = 2e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(\left(2\frac{\text{RU}(0)}{\text{NE}(0)} - \frac{1}{2}\,(2l+1)\right)\frac{P_{\text{inner}}}{\beta}\sin(\frac{k}{2}\beta t) + \frac{1}{2}\cos(\frac{k}{2}\beta t)\right)$$

If $RU(0) \gg \frac{1}{4}\,(2l+1)\,\text{NE}(0) > NE(0)$, then

$$\text{NE}(t) \approx 2e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(2RU(0)\frac{P_{\text{inner}}}{\beta}\sin(\frac{k}{2}\beta t) + \frac{NE(0)}{2}\cos(\frac{k}{2}\beta t)\right) \tag{15}$$

Here, the critical time is

$$t_c = \frac{2}{k\beta}\,\text{arcCot}\left(\left(2l+1-4\frac{RU(0)}{NE(0)}\right)\frac{P_{\text{inner}}}{\beta}\right)$$

For large times $t \gg t_c$, this equation reduces to

$$\text{NE}(t) = 2e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(2\text{RU}(0) - \frac{1}{2}\,(2l+1)\,\text{NE}(0)\right)\frac{P_{\text{inner}}}{\beta}\sin(\frac{k}{2}\beta t) \tag{16}$$

The derivative of $NE(t)$ is in this case

$$\begin{aligned}
\frac{\text{dNE}}{\text{dt}} =& -kP_{\text{inner}}\,(2l+1)\,e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(\left(2\text{RU}(0) - \frac{1}{2}\,(2l+1)\,\text{NE}(0)\right)\frac{P_{\text{inner}}}{\beta}\sin(\frac{k}{2}\beta t) + \frac{NE(0)}{2}\cos(\frac{k}{2}\beta t)\right)\\
&+ 2e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(\left(2\text{RU}(0) - \frac{1}{2}\,(2l+1)\,\text{NE}(0)\right)\frac{P_{\text{inner}}}{\beta}\frac{k}{2}\beta\cos(\frac{k}{2}\beta t) - \frac{NE(0)}{2}\frac{k}{2}\beta\sin(\frac{k}{2}\beta t)\right)\\
=&ke^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}(\left(\left(\frac{1}{2}\,(2l+1)^2\,\frac{P_{\text{inner}}^2}{\beta} - \frac{1}{2}\beta\right)NE(0) - 2\,(2l+1)\,\frac{P_{\text{inner}}^2}{\beta}RU(0)\right)\sin(\frac{k}{2}\beta t)\\
&+ (-\,(2l+1)\,NE(0) + 2RU(0))\,P_{\text{inner}}\cos(\frac{k}{2}\beta t))
\end{aligned} \tag{17}$$

In this case, the function NE(t) has an extreme point at

$$t_1 = \frac{2}{k\beta}\tan^{-1}\left(\frac{((2l+1)\,NE(0)-2RU(0))P_{\text{inner}}}{\left(\frac{1}{2}(2l+1)^2\frac{P_{\text{inner}}^2}{x}-\frac{1}{2}\beta\right)NE(0)-2\,(2l+1)\,\frac{P_{\text{inner}}^2}{x}RU(0)}\right).$$

The function increases monotonically up to t_1 and then decreases to $\lim_{t\to\infty} NE(t) = 0$. At t_1, the degree of polymerization N_P reaches the value of $2l+1$. There is

no chemical bond in a chain of length $2l + 1$ or lower, which can be cutted in two parts without the creation of at least one diffusible fragment. That means, that the probability to create a diffusive fragment ($P_{diff} = \frac{2l}{N_P - 1}$) gets 1 and the opposite probability to create no diffusive fragment ($1 - P_{diff}$) gets 0 at $N_P = 2l + 1$. For $N_P < 2l + 1$, P_{diff} gets bigger than 1 and $1 - P_{diff}$ smaller than 0. Mathematically, a negative probability $1 - P_{diff}$ to have a chain cut within the chain, which increases the number of chain ends by 2, is identical to the situation to have a positive probability $|1 - P_{diff}|$ to decrease the number of chain ends by 2. As a result, the number of chain ends decreases for $t > t_1$.
In reality, probabilities can only have values between 0 and 1. The previous equations are therefore only valid for $0 \leq t < t_1$. It is discussed below, how the model has to be adjusted for $N_P < 2l + 1$. In this case, the number of chain ends decreases, but the reason is different: Chain cuts in oligomers with a length of less than $2l + 1$ have the possibility to create two diffusible fragments with one chain cut. If this happens, the number of chain ends actually decreases by 2, but at the same time the number of repeating units also decreases because the created two diffusible fragments do not count anymore to the molecular mass.
For completeness, Eq. 10 reduces for small times $t \ll t_c$ to

$$\mathrm{NE}(t) = e^{-\frac{kP_{\mathrm{inner}}}{2}(2l+1)t} NE(0) \cos(\frac{k}{2}\beta t) \tag{18}$$

for $P_{\mathrm{inner}} < (4l^2 + 4l)/(4l^2 + 4l + 1)$ and

$$\mathrm{NE}(t) = e^{-\frac{kP_{\mathrm{inner}}}{2}(2l+1)t} NE(0) \cosh(\frac{k}{2}xt) \tag{19}$$

for $P_{\mathrm{inner}} \geq (4l^2 + 4l)/(4l^2 + 4l + 1)$. As expected, $\lim_{t \to 0} NE(t) = NE(0)$. Note, that $t_c < 0$ for $\frac{RU(0)}{NE(0)} > l + \frac{1}{2}$, which means that the approximation for large times is correct as long as the initial configuration contains a polymer, whose oligomers are longer than a diffusible fragment.
For further discussion, it is helpful to know the value of $NE(t_1)$ at its maximum. The calculation is performed for $P_{\mathrm{inner}} \geq (4l^2 + 4l)/(4l^2 + 4l + 1)$. The calculation for $P_{\mathrm{inner}} < (4l^2 + 4l)/(4l^2 + 4l + 1)$ is similar if one replaces x by β and all hyperbolic functions by its nonhyperbolic twin functions.
The value of $NE(t_1)$ is a result of the hyperbolic sine or cosine of the inverse hyperbolic tangent. Let's calculate the inverse hyperbolic tangent first:

$$\tanh(x) = 1 - \frac{2}{e^{2x} + 1}$$
$$\tanh^{-1}(x) = \frac{1}{2} \ln(\frac{1 + x}{1 - x})$$

In our case

$$x_1 = \frac{((2l + 1)\, NE(0) - 2RU(0))P_{\mathrm{inner}}}{\left(\frac{1}{2}(2l + 1)^2 \frac{P_{\mathrm{inner}}^2}{x} + \frac{1}{2}x\right) NE(0) - 2\,(2l + 1)\, \frac{P_{\mathrm{inner}}^2}{x} RU(0)}$$
$$t_1 = \frac{2}{kx} \tanh^{-1}(x_1)$$

The function $NE(t)$ can be rewritten in an hyperbolic tangent:

$$NE(t) = 2e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\cosh(\frac{k}{2}xt)\left(\left(2\text{RU}(0)-\frac{1}{2}(2l+1)\,\text{NE}(0)\right)\frac{P_{\text{inner}}}{x}\tanh(\frac{k}{2}xt)+\frac{NE(0)}{2}\right)$$

Let's calculate the terms separately:

$$\begin{aligned}
\tanh(\frac{k}{2}xt_1) &= x_1\\
\cosh(\frac{k}{2}xt_1) &= \frac{1}{2}\left(e^{\frac{k}{2}xt_1}+e^{-\frac{k}{2}xt_1}\right)\\
&= \frac{1}{2}\left(e^{\frac{1}{2}\ln(\frac{1+x_1}{1-x_1})}+e^{-\frac{1}{2}\ln(\frac{1+x_1}{1-x_1})}\right)\\
&= \frac{1}{2}\left(\left(\frac{1+x_1}{1-x_1}\right)^{\frac{1}{2}}+\left(\frac{1+x_1}{1-x_1}\right)^{-\frac{1}{2}}\right)\\
e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t_1} &= e^{-(2l+1)\frac{P_{\text{inner}}}{x}\frac{1}{2}\ln(\frac{1+x_1}{1-x_1})}\\
&= \left(\frac{1+x_1}{1-x_1}\right)^{-\frac{1}{2}(2l+1)\frac{P_{\text{inner}}}{x}}\\
2e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t_1}\cosh(\frac{k}{2}xt_1) &= \left(\frac{1+x_1}{1-x_1}\right)^{-l-\frac{1}{2}(-1+\frac{P_{\text{inner}}}{x})}+\left(\frac{1+x_1}{1-x_1}\right)^{-l-\frac{1}{2}(1+\frac{P_{\text{inner}}}{x})}\\
&= \frac{\frac{1+x_1}{1-x_1}+1}{\left(\frac{1+x_1}{1-x_1}\right)^{l+\frac{1}{2}(1+\frac{P_{\text{inner}}}{x})}}\\
&= \frac{2}{1+x_1}\left(\frac{1+x_1}{1-x_1}\right)^{-l+\frac{1}{2}(1-\frac{P_{\text{inner}}}{x})}
\end{aligned}$$

$$\begin{aligned}
\frac{1+x_1}{1-x_1} &= \frac{\left(\frac{1}{2}(2l+1)^2\frac{P_{\text{inner}}^2}{x}+\frac{1}{2}x\right)NE(0)-2\,(2l+1)\,\frac{P_{\text{inner}}^2}{x}RU(0)+((2l+1)\,NE(0)-2RU(0))P_{\text{inner}}}{\left(\frac{1}{2}(2l+1)^2\frac{P_{\text{inner}}^2}{x}+\frac{1}{2}x\right)NE(0)-2\,(2l+1)\,\frac{P_{\text{inner}}^2}{x}RU(0)-((2l+1)\,NE(0)-2RU(0))P_{\text{inner}}}\\
&= \frac{\left(\frac{1}{2}(2l+1)^2\frac{P_{\text{inner}}^2}{x}+\frac{1}{2}x+(2l+1)\,P_{\text{inner}}\right)NE(0)-\left(2\,(2l+1)\,\frac{P_{\text{inner}}^2}{x}+2P_{\text{inner}}\right)RU(0)}{\left(\frac{1}{2}(2l+1)^2\frac{P_{\text{inner}}^2}{x}+\frac{1}{2}x-(2l+1)\,P_{\text{inner}}\right)NE(0)-\left(2\,(2l+1)\,\frac{P_{\text{inner}}^2}{x}-2P_{\text{inner}}\right)RU(0)}\\
\frac{2}{1+x_1} &= \frac{\left((2l+1)^2\frac{P_{\text{inner}}^2}{x}+x\right)NE(0)-4\,(2l+1)\,\frac{P_{\text{inner}}^2}{x}RU(0)}{\left(\frac{1}{2}\,(2l+1)^2\,\frac{P_{\text{inner}}^2}{x}+\frac{1}{2}x+(2l+1)\,P_{\text{inner}}\right)NE(0)-\left(2\,(2l+1)\,\frac{P_{\text{inner}}^2}{x}+2P_{\text{inner}}\right)RU(0)}
\end{aligned}$$

We get for the maximum number of chain ends of a random chain cut mechanism

$$NE(t_1) = ABC$$

$$A = \frac{\left((2l+1)^2 \frac{P_{\text{inner}}^2}{x} + x\right) NE(0) - 4\,(2l+1)\,\frac{P_{\text{inner}}^2}{x} RU(0)}{\left(\frac{1}{2}\,(2l+1)^2\,\frac{P_{\text{inner}}^2}{x} + \frac{1}{2}x + (2l+1)\,P_{\text{inner}}\right) NE(0) - \left(2\,(2l+1)\,\frac{P_{\text{inner}}^2}{x} + 2P_{\text{inner}}\right) RU(0)}$$

$$B = \left(\frac{\left(\frac{1}{2}(2l+1)^2\frac{P_{\text{inner}}^2}{x} + \frac{1}{2}x\right) NE(0) - 2\,(2l+1)\,\frac{P_{\text{inner}}^2}{x} RU(0) + ((2l+1)\,NE(0) - 2RU(0))P_{\text{inner}}}{\left(\frac{1}{2}(2l+1)^2\frac{P_{\text{inner}}^2}{x} + \frac{1}{2}x\right) NE(0) - 2\,(2l+1)\,\frac{P_{\text{inner}}^2}{x} RU(0) - ((2l+1)\,NE(0) - 2RU(0))P_{\text{inner}}}\right)^{-l+\frac{1}{2}(1-\frac{P_{\text{inner}}}{x})}$$

$$C = \left(\left(2\mathrm{RU}(0) - \frac{1}{2}\,(2l+1)\,\mathrm{NE}(0)\right)\frac{P_{\text{inner}}^2}{x}\,\frac{((2l+1)\,NE(0) - 2RU(0))}{\left(\frac{1}{2}(2l+1)^2\frac{P_{\text{inner}}^2}{x} + \frac{1}{2}x\right) NE(0) - 2\,(2l+1)\,\frac{P_{\text{inner}}^2}{x} RU(0)} + \frac{NE(0)}{2}\right)$$

$$NE(t_1) = \frac{((4l+2)\,RU(0)NE(0) - (l\,(l+1) + \frac{1}{4})NE(0)^2 - 4RU(0)^2)\,\frac{P_{\text{inner}}^2}{x} + \frac{1}{4}xNE(0)^2}{\left(\frac{1}{4}\,(2l+1)^2\,\frac{P_{\text{inner}}^2}{x} + \frac{1}{4}x + \frac{1}{2}\,(2l+1)\,P_{\text{inner}}\right) NE(0) - \left((2l+1)\,\frac{P_{\text{inner}}^2}{x} + P_{\text{inner}}\right) RU(0)} B$$

For large chains at the beginning of the degradation ($RU(0) \gg NE(0)$), the maximum value is approximately

$$\lim_{\frac{RU(0)}{NE(0)}\to\infty} NE(t_1) = \frac{4}{2l+1+\frac{x}{P_{\text{inner}}}}\left(\frac{(2l+1)\frac{P_{\text{inner}}}{x} - 1}{(2l+1)\frac{P_{\text{inner}}}{x} + 1}\right)^{l-\frac{1}{2}(1-\frac{P_{\text{inner}}}{x})}$$

1.2 Number of repeating units

Now, let's turn to the number of repeating units. Using Eq. 3, we can directly write

$$\mathrm{RU}(t) = \frac{1}{2kP_{\text{inner}}}\frac{\mathrm{dNE}}{\mathrm{d}t} + \frac{1}{2}\,(2l+1)\,NE \tag{20}$$

Using Eqs. 13 and 10 one can write

$$\begin{aligned}
\mathrm{RU}(t) = \frac{1}{2kP_{\text{inner}}}(\quad & ke^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}(\left(\left(\frac{1}{2}\,(2l+1)^2\,\frac{P_{\text{inner}}^2}{x} + \frac{1}{2}x\right) NE(0) - 2\,(2l+1)\,\frac{P_{\text{inner}}^2}{x} RU(0)\right)\sinh(\frac{k}{2}xt) \\
& + (-\,(2l+1)\,NE(0) + 2RU(0))\,P_{\text{inner}}\cosh(\frac{k}{2}xt)) \\
+\,\frac{1}{2}\,(2l+1) \quad & \left(2e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(\left(2\mathrm{RU}(0) - \frac{1}{2}\,(2l+1)\,\mathrm{NE}(0)\right)\frac{P_{\text{inner}}}{x}\sinh(\frac{k}{2}xt) + \frac{NE(0)}{2}\cosh(\frac{k}{2}xt)\right)\right) \\
= e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t} & \left(\left((2l+1)\,\frac{P_{\text{inner}}}{x} RU(0) + \frac{1}{4}\left(x - (2l+1)^2\,\frac{P_{\text{inner}}}{x}\right) NE(0)\right)\sinh(\frac{k}{2}xt) + \mathrm{RU}(0)\cosh(\frac{k}{2}xt)\right)
\end{aligned} \tag{21}$$

for $P_{\text{inner}} \geq (4l^2+4l)/(4l^2+4l+1)$. For $P_{\text{inner}} < (4l^2+4l)/(4l^2+4l+1)$, we get

$$\begin{aligned}
\mathrm{RU}(t) = e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}(& \left((2l+1)\,\frac{P_{\text{inner}}}{\beta} RU(0) + \frac{1}{4}\left(-\beta - (2l+1)^2\,\frac{P_{\text{inner}}}{\beta}\right) NE(0)\right)\sin(\frac{k}{2}\beta t) \\
& + \mathrm{RU}(0)\cos(\frac{k}{2}\beta t))
\end{aligned}$$

The function converges to $\lim_{t\to 0} RU(t) = RU(0)$ as expected. The derivative of this function is

$$\frac{\mathrm{dRU}}{\mathrm{d}t} = -\frac{kP_{\mathrm{inner}}}{2}(2l+1)\,e^{-\frac{kP_{\mathrm{inner}}}{2}(2l+1)t}\left(\left((2l+1)\frac{P_{\mathrm{inner}}}{x}RU(0)+\frac{1}{4}\left(x-(2l+1)^2\frac{P_{\mathrm{inner}}}{x}\right)NE(0)\right)\sinh(\frac{k}{2}xt)+\mathrm{RU}(0)\cosh(\frac{k}{2}xt)\right)$$
$$+\,e^{-\frac{kP_{\mathrm{inner}}}{2}(2l+1)t}\left(\left((2l+1)\frac{P_{\mathrm{inner}}}{x}RU(0)+\frac{1}{4}\left(x-(2l+1)^2\frac{P_{\mathrm{inner}}}{x}\right)NE(0)\right)\frac{k}{2}x\cosh(\frac{k}{2}xt)+\mathrm{RU}(0)\frac{k}{2}x\sinh(\frac{k}{2}xt)\right)$$
$$=\frac{k}{2}e^{-\frac{kP_{\mathrm{inner}}}{2}(2l+1)t}\Big(\left(\frac{1}{4}\left((2l+1)^3\frac{P^2_{\mathrm{inner}}}{x}-(2l+1)\,xP_{\mathrm{inner}}\right)NE(0)+\left(x-(2l+1)^2\frac{P^2_{\mathrm{inner}}}{x}\right)RU(0)\right)\sinh(\frac{k}{2}xt)$$
$$+\left(\frac{1}{4}\left(x-(2l+1)^2\frac{P_{\mathrm{inner}}}{x}\right)NE(0)+(2l+1)\left(\frac{P_{\mathrm{inner}}}{x}-\frac{1}{2}P_{\mathrm{inner}}\right)RU(0)\right)\cosh(\frac{k}{2}xt)\Big) \qquad (22)$$

for $P_{\mathrm{inner}} \geq (4l^2+4l)/(4l^2+4l+1)$ and

$$\frac{\mathrm{dRU}}{\mathrm{d}t} = \frac{k}{2}e^{-\frac{kP_{\mathrm{inner}}}{2}(2l+1)t}\Big(\left(\frac{1}{4}\left((2l+1)^3\frac{P^2_{\mathrm{inner}}}{\beta}+(2l+1)\,\beta P_{\mathrm{inner}}\right)NE(0)+\left(-\beta-(2l+1)^2\frac{P^2_{\mathrm{inner}}}{\beta}\right)RU(0)\right)\sin(\frac{k}{2}\beta t)$$
$$+\left(\frac{1}{4}\left(-\beta-(2l+1)^2\frac{P_{\mathrm{inner}}}{\beta}\right)NE(0)+(2l+1)\left(\frac{P_{\mathrm{inner}}}{\beta}-\frac{1}{2}P_{\mathrm{inner}}\right)RU(0)\right)\cos(\frac{k}{2}\beta t)\Big)$$

for $P_{\mathrm{inner}} < (4l^2+4l)/(4l^2+4l+1)$. Now the number of repeating units at t_1 is calculated. $RU(t)$ is written in hyperbolic tangent form:

$$\mathrm{RU}(t) = e^{-\frac{kP_{\mathrm{inner}}}{2}(2l+1)t}\cosh(\frac{k}{2}xt)\left(\left((2l+1)\frac{P_{\mathrm{inner}}}{x}RU(0)+\frac{1}{4}\left(x-(2l+1)^2\frac{P_{\mathrm{inner}}}{x}\right)NE(0)\right)\tanh(\frac{k}{2}xt)+\mathrm{RU}(0)\right) \qquad (23)$$

for $P_{\mathrm{inner}} \geq (4l^2+4l)/(4l^2+4l+1)$ and

$$\mathrm{RU}(t) = e^{-\frac{kP_{\mathrm{inner}}}{2}(2l+1)t}\cos(\frac{k}{2}\beta t)\left(\left((2l+1)\frac{P_{\mathrm{inner}}}{\beta}RU(0)+\frac{1}{4}\left(-\beta-(2l+1)^2\frac{P_{\mathrm{inner}}}{\beta}\right)NE(0)\right)\tan(\frac{k}{2}\beta t)+\mathrm{RU}(0)\right) \qquad (24)$$

for $P_{\mathrm{inner}} < (4l^2+4l)/(4l^2+4l+1)$. The value at t_1 is:

$$RU(t_1) = \frac{1}{2}ABC_R$$
$$A = \frac{\left((2l+1)^2\frac{P^2_{\mathrm{inner}}}{x}+x\right)NE(0)-4\,(2l+1)\frac{P^2_{\mathrm{inner}}}{x}RU(0)}{\left(\frac{1}{2}(2l+1)^2\frac{P^2_{\mathrm{inner}}}{x}+\frac{1}{2}x+(2l+1)\,P_{\mathrm{inner}}\right)NE(0)-\left(2\,(2l+1)\frac{P^2_{\mathrm{inner}}}{x}+2P_{\mathrm{inner}}\right)RU(0)}$$
$$B = \left(\frac{\left(\frac{1}{2}(2l+1)^2\frac{P^2_{\mathrm{inner}}}{x}+\frac{1}{2}x\right)NE(0)-2\,(2l+1)\frac{P^2_{\mathrm{inner}}}{x}RU(0)+((2l+1)\,NE(0)-2RU(0))P_{\mathrm{inner}}}{\left(\frac{1}{2}(2l+1)^2\frac{P^2_{\mathrm{inner}}}{x}+\frac{1}{2}x\right)NE(0)-2\,(2l+1)\frac{P^2_{\mathrm{inner}}}{x}RU(0)-((2l+1)\,NE(0)-2RU(0))P_{\mathrm{inner}}}\right)^{-l+\frac{1}{2}(1-\frac{P_{\mathrm{inner}}}{x})}$$
$$C_R = \left((2l+1)\frac{P_{\mathrm{inner}}}{x}RU(0)+\frac{1}{4}\left(x-(2l+1)^2\frac{P_{\mathrm{inner}}}{x}\right)NE(0)\right)\frac{((2l+1)\,NE(0)-2RU(0))P_{\mathrm{inner}}}{\left(\frac{1}{2}(2l+1)^2\frac{P^2_{\mathrm{inner}}}{x}+\frac{1}{2}x\right)NE(0)-2\,(2l+1)\frac{P^2_{\mathrm{inner}}}{x}RU(0)}+\mathrm{RU}(0)$$
$$RU(t_1) = \frac{(2l+1)^2\frac{P^2_{\mathrm{inner}}}{x}RU(0)NE(0)+\frac{1}{8}(2l+1)\left(x-(2l+1)^2\frac{P^2_{\mathrm{inner}}}{x}\right)NE(0)^2-2\,(2l+1)\frac{P^2_{\mathrm{inner}}}{x}RU(0)^2}{\left(\frac{1}{4}(2l+1)^2\frac{P^2_{\mathrm{inner}}}{x}+\frac{1}{4}x+\frac{1}{2}(2l+1)\,P_{\mathrm{inner}}\right)NE(0)-\left((2l+1)\frac{P^2_{\mathrm{inner}}}{x}+P_{\mathrm{inner}}\right)RU(0)}B$$

for $P_{\mathrm{inner}} \geq (4l^2+4l)/(4l^2+4l+1)$. For large chains at the beginning of the degradation ($RU(0) \gg NE(0)$), the number of repeating units for $N_P = 2l+1$ is approximately

$$\lim_{\frac{RU(0)}{NE(0)}\to\infty} RU(t_1) = \frac{4l+2}{2l+1+\frac{x}{P_{\mathrm{inner}}}}\left(\frac{(2l+1)\frac{P_{\mathrm{inner}}}{x}-1}{(2l+1)\frac{P_{\mathrm{inner}}}{x}+1}\right)^{l-\frac{1}{2}(1-\frac{P_{\mathrm{inner}}}{x})}$$

1.3 Degree of polymerization

Eqs. 10 and 20 are used to calculate the degree of polymerization

$$\begin{aligned}
\mathrm{N_P}(t) &= \frac{RU}{\frac{NE}{2}} \\
&= 2l+1+\frac{\frac{\mathrm{dNE}}{\mathrm{d}t}}{kP_{\mathrm{inner}}NE} \\
&= 2l+1+\frac{\left(\left(\frac{1}{2}\,(2l+1)^2\,\frac{P_{\mathrm{inner}}}{x}+\frac{1}{2}\,\frac{x}{P_{\mathrm{innner}}}\right)NE(0)-2\,(2l+1)\,\frac{P_{\mathrm{inner}}}{x}\,RU(0)\right)\sinh(\frac{k}{2}xt)+(-\,(2l+1)\,NE(0)+2RU(0))\cosh(\frac{k}{2}xt)}{2\left(\left(2\mathrm{RU}(0)-\frac{1}{2}\,(2l+1)\,\mathrm{NE}(0)\right)\frac{P_{\mathrm{inner}}}{x}\sinh(\frac{k}{2}xt)+\frac{NE(0)}{2}\cosh(\frac{k}{2}xt)\right)}
\end{aligned} \tag{25}$$

The function converges to $\lim_{t\to 0} N_P(t) = 2\frac{RU(0)}{NE(0)}$ as expected.

2 Degradation curve for l+1 < N_P < 2l+1

2.1 Number of chain ends and repeating units

If the length of an oligomer is lower or equal to 2l+1, every chain cut will create at least one diffusive fragment. In case of length 2l+1, exactly one diffusive fragment is created, which reduces the number of RU by the average length of a diffusive fragment $(l + \frac{1}{2})$ and does not change the number of chain ends NE. If the oligomers are smaller than 2l+1, chain cuts in the center of these oligomers are possible, which divide the oligomer in two diffusive fragments. For such a chain cut, the complete oligomer is degraded, which means that the number of chain ends decreases by 2 and the number of RUs decreases by the degree of polymerization N_P. The probability for such a chain cut in an oligomer of length $N_P \leq$ 2l+1 is $P_{doublecut} = \frac{2l+1-N_P}{N_P-1}$. Similarly, the probability to have a chain cut in an oligomer of length smaller or equal to 2l+1, which creates only one diffusible fragment, is $1 - P_{doublecut}$. The corresponding equations are

$$\begin{aligned}\frac{\mathrm{dNE}^*}{\mathrm{d}t'} &= k\left(\mathrm{RU}^* - \frac{\mathrm{NE}^*}{2}\right)\left(-2\frac{2l+1-N_P}{N_P-1}\right) \\ &= kNE^*(2\frac{RU^*}{NE^*} - 2l - 1) \\ &= k(2RU^* - NE^*(2l+1)) \end{aligned} \tag{26}$$

and

$$\begin{aligned}\frac{\mathrm{dRU}^*}{\mathrm{d}t'} &= -k\left(\mathrm{RU}^* - \frac{\mathrm{NE}^*}{2}\right)\left(\frac{2l+1-N_P}{N_P-1}N_P + \left(1 - \frac{2l+1-N_P}{N_P-1}\right)\frac{1}{2}(l+1)\right) \\ &= -k\left(\mathrm{RU}^* - \frac{\mathrm{NE}^*}{2}\right)\left(\frac{2l+1-N_P}{N_P-1}N_P + \frac{1}{2}\frac{2N_P-2l-2}{N_P-1}(l+1)\right) \\ &= k\frac{\mathrm{NE}^*}{2}\left(N_P^2 - (3l+2)N_P + l^2 + 2l + 1\right) \\ &= k\left(2\frac{RU^{*2}}{NE^*} - (3l+2)RU^* + \frac{1}{2}l^2NE^* + lNE^* + \frac{1}{2}NE^*\right) \end{aligned} \tag{27}$$

Note, that we write NE^* and RU^* instead of NE and RU to differentiate the functions from the previous ones. Furthermore, we introduce the time $t' = t - t_1$ because we consider a degradation process, which starts at $t = t_1$ with initial number of chain ends $NE(t_1) = NE(t' = 0)$ and repeating units $RU(t_1) = RU(t' = 0)$. Interestingly, equation 26 is identical to 3 (except for P_{inner}). However, the solution is different because $RU^*(t')$ is different. Eq. 27 is not easily analytically solvable because it contains $NE^*(t')$ in the denominator and RU^* in second order. The reason is that the number of repeating units changes by N_P in a chain cut, which creates two diffusible fragments. As N_P is the average degree of polymerization, we can replace it by the average length of an oligomer, which creates diffusible fragments. The shortest length of such an oligomer is l+1 (1 RU longer than a diffusive fragment) and the longest length is 2l. The average length is therefore

$\frac{1}{2}(3l+1)$. This means that the differential equation changes to

$$\begin{aligned}
\frac{\mathrm{dRU}^*}{\mathrm{d}t'} &= -k\left(\mathrm{RU}^* - \frac{\mathrm{NE}^*}{2}\right)\left(\frac{2l+1-N_P}{N_P-1}\frac{1}{2}(3l+1) + \left(1 - \frac{2l+1-N_P}{N_P-1}\right)\frac{1}{2}(l+1)\right) \\
&= -k\left(\mathrm{RU}^* - \frac{\mathrm{NE}^*}{2}\right)\left(\frac{2l+1-N_P}{N_P-1}\frac{1}{2}(3l+1) + \frac{1}{2}\frac{2N_P-2l-2}{N_P-1}(l+1)\right) \\
&= -k\frac{\mathrm{NE}^*}{4}\left((-l+1)N_P + 4l^2 + l - 1\right) \\
&= k\left(\frac{1}{2}(l-1)RU^* - NE^*l^2 + \frac{1}{4}NE^*(-l+1)\right) \\
&= k\left(\frac{1}{2}(l-1)RU^* + \frac{1}{4}NE^*\left(-4l^2 - l + 1\right)\right) \qquad (28)
\end{aligned}$$

This differential equation is linear in RU^* and NE^* and therefore analytically solvable. We write the system of coupled linear differential equations in matrix form:

$$\begin{aligned}
\begin{pmatrix} \frac{\mathrm{dNE}^*}{\mathrm{d}t'} \\ \frac{\mathrm{dRU}^*}{\mathrm{d}t'} \end{pmatrix} &= k\begin{pmatrix} -(2l+1) & 2 \\ \frac{1}{4}\left(-4l^2 - l + 1\right) & \frac{1}{2}(l-1) \end{pmatrix}\begin{pmatrix} NE^* \\ RU^* \end{pmatrix} \\
&= A\begin{pmatrix} NE^* \\ RU^* \end{pmatrix}
\end{aligned}$$

A general solution is a linear combination of the eigenvectors $\mathbf{v}_1$ and $\mathbf{v}_2$ with its corresponding eigenvalues λ_1 and λ_2, respectively.

$$\begin{pmatrix} NE^* \\ RU^* \end{pmatrix} = Ce^{\lambda_1 t'}\mathbf{v}_1 + De^{\lambda_2 t'}\mathbf{v}_2$$

One can write matrix A in the form

$$A = k\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$$

The eigenvalues of matrix A are

$$\lambda_{1/2} = \frac{1}{2}\operatorname{Tr} A \pm \frac{1}{2}\sqrt{(\operatorname{Tr} A)^2 - 4\det A}$$

with $\operatorname{Tr} A = k(a_{11} + a_{22})$ the trace and $\det A = k^2P^2(a_{11}a_{22} - a_{12}a_{21})$ the determinant of matrix A. An eigenvector to eigenvalue $\lambda_{1/2}$ is

$$\mathbf{v}_{1/2} = \begin{pmatrix} \lambda_{1/2} - a_{22} \\ a_{21} \end{pmatrix}$$

The individual solutions for eigenvalues $\lambda_{1/2} = \alpha \pm i\beta$, are

$$\begin{pmatrix} NE^*_{1/2} \\ RU^*_{1/2} \end{pmatrix} = C_{1/2}\mathbf{v}_{1/2}e^{\alpha t'}e^{\pm i\beta t'}$$

and the general solution is

$$\begin{pmatrix} NE^* \\ RU^* \end{pmatrix} = C_1\mathbf{v}_1e^{\alpha t'}e^{i\beta t'} + C_2\mathbf{v}_2e^{\alpha t'}e^{-i\beta t'}$$

We are only interested in real solutions $NE^*(t)$, which implies that the constant C_2 has to be the complex conjugate of C_1 (note: $\mathbf{v}_1$ is the complex conjugate of $\mathbf{v}_2$). We set

$$\begin{aligned} C_1 &= \bar{C_2} = \frac{1}{2}C \\ \mathbf{v}_1 &= \bar{\mathbf{v}}_2 = \mathbf{v} \end{aligned}$$

With the new constant C and vector $\mathbf{v}$, we can rewrite

$$\begin{pmatrix} NE^* \\ RU^* \end{pmatrix} = \Re\Big(C\mathbf{v}e^{\alpha t'}e^{i\beta t'}\Big)$$

Now we can write

$$\begin{aligned} \begin{pmatrix} NE^* \\ RU^* \end{pmatrix} &= e^{\alpha t'}\Re\Big((\Re(C) + i\Im(C))\left(\cos\left(\beta t'\right) + i\sin\left(\beta t'\right)\right)\begin{pmatrix} \alpha + i\beta - a_{22} \\ a_{21} \end{pmatrix}\Big) \\ &= e^{\alpha t'}\Re\Big((\Re(C) + i\Im(C))\begin{pmatrix} (\alpha - a_{22})\cos\left(\beta t'\right) - \beta\sin\left(\beta t'\right) \\ a_{21}\cos\left(\beta t'\right) \end{pmatrix} + i\begin{pmatrix} (\alpha - a_{22})\sin\left(\beta t'\right) + \beta\cos\left(\beta t'\right) \\ a_{21}\sin\left(\beta t'\right) \end{pmatrix}\Big) \\ \mathbf{w} &= \begin{pmatrix} (\alpha - a_{22})\cos\left(\beta t'\right) - \beta\sin\left(\beta t'\right) \\ a_{21}\cos\left(\beta t'\right) \end{pmatrix} + i\begin{pmatrix} (\alpha - a_{22})\sin\left(\beta t'\right) + \beta\cos\left(\beta t'\right) \\ a_{21}\sin\left(\beta t'\right) \end{pmatrix} \\ \begin{pmatrix} NE^* \\ RU^* \end{pmatrix} &= e^{\alpha t'}\Re((\Re(C) + i\Im(C))\left(\Re(\mathbf{w}) + i\Im(\mathbf{w})\right)) \\ &= e^{\alpha t'}\Re((\Re(C)\Re(\mathbf{w}) - \Im(C)\Im(\mathbf{w})) + i\left(\Re(C)\Im(\mathbf{w}) + \Im(C)\Re(\mathbf{w})\right)) \\ &= e^{\alpha t'}\left(\Re(C)\Re(\mathbf{w}) - \Im(C)\Im(\mathbf{w})\right) \end{aligned}$$

The real and imaginary part of the complex constant C are individual real constants. We set $X = \Re(C)$ and $Y = -\Im(C)$ and get

$$\begin{pmatrix} NE^* \\ RU^* \end{pmatrix} = e^{\alpha t'}\left(X\begin{pmatrix} (\alpha - a_{22})\cos\left(\beta t'\right) - \beta\sin\left(\beta t'\right) \\ a_{21}\cos\left(\beta t'\right) \end{pmatrix} + Y\begin{pmatrix} (\alpha - a_{22})\sin\left(\beta t'\right) + \beta\cos\left(\beta t'\right) \\ a_{21}\sin\left(\beta t'\right) \end{pmatrix}\right)$$

We determine the real constants X and Y with the help of the initial conditions:

$$\begin{pmatrix} NE^*(0) \\ RU^*(0) \end{pmatrix} = \left(X\begin{pmatrix} \alpha - a_{22} \\ a_{21} \end{pmatrix} + Y\begin{pmatrix} \beta \\ 0 \end{pmatrix}\right)$$

which leads to

$$\begin{aligned} X &= \frac{RU^*(0)}{a_{21}} \\ Y &= \frac{1}{\beta}NE^*(0) + \frac{a_{22} - \alpha}{a_{21}\beta}RU^*(0) \end{aligned}$$

This leads to the general solution of a coupled system of two linear ordinary differential equations:

$$\begin{aligned} \begin{pmatrix} NE^* \\ RU^* \end{pmatrix} = e^{\alpha t'}(&\frac{RU^*(0)}{a_{21}}\begin{pmatrix} (\alpha - a_{22})\cos\left(\beta t'\right) - \beta\sin\left(\beta t'\right) \\ a_{21}\cos\left(\beta t'\right) \end{pmatrix} \\ &+ \frac{a_{21}NE^*(0) + (a_{22} - \alpha)\,RU^*(0)}{a_{21}\beta}\begin{pmatrix} (\alpha - a_{22})\sin\left(\beta t'\right) + \beta\cos\left(\beta t'\right) \\ a_{21}\sin\left(\beta t'\right) \end{pmatrix}) \end{aligned}$$

The derivatives are

$$\begin{pmatrix} \frac{\mathrm{dNE}^*}{\mathrm{d}t'} \\ \frac{\mathrm{dRU}^*}{\mathrm{d}t'} \end{pmatrix} = e^{\alpha t'} (\frac{RU^*(0)}{a_{21}} \begin{pmatrix} \left(\alpha^2 - a_{22}\alpha - \beta^2\right)\cos\left(\beta t'\right) + \left(\beta a_{22} - 2\alpha\beta\right)\sin\left(\beta t'\right) \\ \alpha a_{21}\cos\left(\beta t'\right) - \beta a_{21}\sin\left(\beta t'\right) \end{pmatrix}$$
$$+ \frac{a_{21}NE^*(0) + \left(a_{22} - \alpha\right)RU^*(0)}{a_{21}\beta} \begin{pmatrix} \left(2\alpha\beta - \beta a_{22}\right)\cos\left(\beta t'\right) + \left(\alpha^2 - \alpha a_{22} - \beta^2\right)\sin\left(\beta t'\right) \\ \beta a_{21}\cos\left(\beta t'\right) + \alpha a_{21}\sin\left(\beta t'\right) \end{pmatrix})$$

In the derivative, we get a term which depends on β^2. Because β represents the imaginary part of the eigenvalue λ, $\beta^2 = -|\beta|^2$. Then we get for the derivatives at $t' = 0$ the expected result:

$$\begin{pmatrix} \frac{\mathrm{dNE}^*}{\mathrm{d}t'}(0) \\ \frac{\mathrm{dRU}^*}{\mathrm{d}t'}(0) \end{pmatrix} = \begin{pmatrix} a_{11}NE^*(0) + a_{12}RU^*(0) \\ a_{21}NE^*(0) + a_{22}RU^*(0) \end{pmatrix}$$

We rewrite our functions:

$$\begin{aligned} \begin{pmatrix} NE^* \\ RU^* \end{pmatrix} &= B \begin{pmatrix} NE^*(0) \\ RU^*(0) \end{pmatrix} \\ &= e^{\alpha t'} \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} \begin{pmatrix} NE^*(0) \\ RU^*(0) \end{pmatrix} \end{aligned}$$

with

$$b_{11} = \frac{\alpha - a_{22}}{\beta}\sin\left(\beta t'\right) + \cos\left(\beta t'\right) \tag{29}$$

$$b_{12} = \left(-\frac{\beta}{a_{21}} - \frac{\left(\alpha - a_{22}\right)^2}{a_{21}\beta}\right)\sin\left(\beta t'\right) \tag{30}$$

$$b_{21} = \frac{a_{21}}{\beta}\sin\left(\beta t'\right) \tag{31}$$

$$b_{22} = \frac{a_{22} - \alpha}{\beta}\sin\left(\beta t'\right) + \cos\left(\beta t'\right) \tag{32}$$

In our specific case $a_{11} = -2l - 1$, $a_{12} = 2$, $a_{21} = \frac{1}{4}\left(-4l^2 - l + 1\right)$ and $a_{22} = \frac{1}{2}\left(l - 1\right)$, $NE^*(t' = 0) = NE(t_1)$ and $RU^*(t' = 0) = RU(t_1)$. Now we calculate explicitly

$$
\begin{aligned}
\mathrm{Tr}\, A &= k\left(-2l-1+\frac{1}{2}\left(l-1\right)\right)\\
&= k\left(-\frac{3}{2}l-\frac{3}{2}\right)\\
\det A &= k^2P^2\left(\left(-2l-1\right)\frac{1}{2}\left(l-1\right)-2\frac{1}{4}\left(-4l^2-l+1\right)\right)\\
&= k^2P^2(l^2+l)\\
\sqrt{\left(\mathrm{Tr}\, A\right)^2-4\det A} &= \frac{ik}{2}\sqrt{7l^2-2l-9}\\
\lambda_{1/2} &= \frac{3k}{4}\left(l+1\right)\pm\frac{ik}{2}\sqrt{7l^2-2l-9}\\
\alpha &= -\frac{3k}{4}\left(l+1\right)\\
\beta &= \frac{k}{2i}\sqrt{7l^2-2l-9}
\end{aligned}
$$

We already calculated the time $t_1(t'=0)$ and the value of the number of chain ends $\mathrm{NE}(t_1)$ and repeating units $\mathrm{RU}(t_1)$. The final solutions are

$$
NE(t)=\begin{cases}2e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(\left(2\mathrm{RU}(0)-\frac{1}{2}\left(2l+1\right)\mathrm{NE}(0)\right)\frac{P_{\text{inner}}}{x}\sinh(\frac{k}{2}xt)+\frac{NE(0)}{2}\cosh(\frac{k}{2}xt)\right) & t\le t_1\\ b_{11}(t-t_1)NE(t_1)+b_{12}(t-t_1)RU(t_1) & t>t_1\end{cases} \tag{33}
$$

$$
RU(t)=\begin{cases}e^{-\frac{kP_{\text{inner}}}{2}(2l+1)t}\left(\left((2l+1)\frac{P_{\text{inner}}}{x}RU(0)+\frac{1}{4}\left(x-(2l+1)^2\frac{P_{\text{inner}}}{x}\right)NE(0)\right)\sinh(\frac{k}{2}xt)+\mathrm{RU}(0)\cosh(\frac{k}{2}xt)\right) & t\le t_1\\ b_{21}(t-t_1)NE(t_1)+b_{22}(t-t_1)RU(t_1) & t>t_1\end{cases} \tag{34}
$$

with $b_{11}(t)$, $b_{12}(t)$, $b_{21}(t)$ and $b_{22}(t)$ from equations (29) to (32).

2.2 Degree of polymerization

With the help of equations (33) and (34), one can directly calculate the degree of polymerization

$$
\begin{aligned}
N_P(t) &= \frac{RU}{\frac{NE}{2}}\\
&= \begin{cases}2l+1+\dfrac{\left(\left(\frac{1}{2}(2l+1)^2\frac{P_{\text{inner}}^2}{x}+\frac{1}{2}x\right)NE(0)-2(2l+1)\frac{P_{\text{inner}}^2}{x}RU(0)\right)\sinh(\frac{k}{2}xt)+(-(2l+1)NE(0)+2RU(0))P_{\text{inner}}\cosh(\frac{k}{2}xt)}{2\left(\left(2\mathrm{RU}(0)-\frac{1}{2}(2l+1)\mathrm{NE}(0)\right)\frac{P_{\text{inner}}}{x}\sinh(\frac{k}{2}xt)+\frac{NE(0)}{2}\cosh(\frac{k}{2}xt)\right)} & t\le t_1\\ \dfrac{2b_{21}(t-t_1)NE(t_1)+2b_{22}(t-t_1)RU(t_1)}{b_{11}(t-t_1)NE(t_1)+b_{12}(t-t_1)RU(t_1)} & t>t_1\end{cases}
\end{aligned} \tag{35}
$$

The second part of the degradation is only valid until the degree of polymerization decreases to a length of a diffusible fragment+1 ($N_P=l+1$). The function reaches this point at

$$
t_2=t_1+\frac{1}{\beta}\arctan\left(\beta\frac{\left(l+1\right)NE^*(0)-2RU^*(0)}{\left(2a_{21}-\left(l+1\right)\left(\alpha-a_{22}\right)\right)NE^*(0)+\left(2\left(a_{22}-\alpha\right)+\left(l+1\right)\left(\alpha-a_{22}\right)^2\right)}\right)
$$

We can therefore calculate the number of chain ends $NE(t_2)$ and repeating units $RU(t_2)$ for the moment when $N_P=l+1$.

3 Degradation curve for $N_P \leq$ l+1

The previous section describes the degradation up to a degree of polymerization of $N_P = l + 1$. At this point, the oligomers are so short, that they can cut a diffusible fragment without being completely degraded. This means, that the probability to have a single cut of a diffusible fragment gets 0 and the probability to have a chain cut, which degrades the remaining oligomer completely into two diffusible fragments gets 1. Furthermore, the number of breakable bonds before a chain cut is

$$\begin{aligned} RU^{**} - \frac{NE^{**}}{2} &= RU^{**}(1 - \frac{\frac{NE^{**}}{2}}{RU^{**}}) \\ &= RU^{**}(1 - \frac{1}{l+1}) \\ &= \frac{l}{l+1} RU^{**} \end{aligned}$$

The number of RUs per chain cut, which is removed from the system, is always $l + 1$ because shorter oligomers are already diffusible fragments. That means, that in this case the differential equations are

$$\begin{aligned} \frac{\mathrm{dNE}^{**}}{\mathrm{d}t} &= k\frac{l}{l+1} RU^{**}\,(-2) \\ &= -2k\frac{l}{l+1} RU^{**} \\ \frac{\mathrm{dRU}^{**}}{\mathrm{d}t} &= -k\frac{l}{l+1} RU^{**}\,(l+1) \\ &= -klRU^{**} \end{aligned}$$

We use the approach

$$RU^{**}(t) = ae^{b(t-t_2)}$$

We get

$$\frac{\mathrm{dRU}^{**}}{\mathrm{d}t} = abe^{b(t-t2)} \tag{36}$$

$$= -klae^{b(t-t_2)} \tag{37}$$

$$\tag{38}$$

and therefore b=-kl. At t=t_2, we get

$$RU^{**}(t_2) = a \tag{39}$$

and therefore a = $RU(t_2)$ because $RU^{**}(t_2) = RU(t_2)$. We have

$$RU^{**}(t) = RU(t_2)e^{-kl(t-t_2)} \tag{40}$$

Now we solve NE(t)

$$\frac{\mathrm{dNE}^{**}}{\mathrm{d}t} = -2k\frac{l}{l+1} RU(t_2)e^{-kl(t-t_2)}$$

Again, we use the approach

$$NE^{**}(t) = ae^{b(t-t_2)} + c$$

We get

$$\frac{\mathrm{dNE}^{**}}{\mathrm{d}t} = abe^{b(t-t_2)}$$

and therefore b=-kl and a=$\frac{2}{l+1}RU(t_2)$. At $t = t_2$, we get

$$NE(t_2) = a + c$$

and therefore c = $NE(t_2)$-$\frac{2}{l+1}RU(t_2)$. So we get finally

$$NE^{**}(t) = \frac{2}{l+1}RU(t_2)e^{-kl(t-t_2)} + NE(t_2) - \frac{2}{l+1}RU(t_2) \tag{41}$$

Here, we set $NE^{**}(t_2) = NE(t_2)$ and $RU^{**}(t_2) = RU(t_2)$ because the function is a continuation of the previous function. These parts of the function describe the degradation of the remaining oligomers of length $l + 1$ in diffusible fragments. However, they are strictly only defined until $RU(t) = l$ because fragments with less than l repeating units are already diffusible fragments. The time when this happens is

$$t_3 = t_2 - \frac{1}{kl} \ln\left(\frac{l}{RU(t_2)}\right)$$

At this point, degradation of the chain in diffusible fragments is completed. The degree of polymerization for the last part is always

$$\begin{aligned} N_P &= \frac{RU}{\frac{NE}{2}} \\ &= l + 1 \end{aligned}$$

for all $t_2 \leq t < t_3$. The full degradation curves are therefore

$$NE(t) = \begin{cases} 2e^{-\frac{k}{2}(2l+1)t}\left(\left(2\mathrm{RU}(0) - \frac{1}{2}(2l+1)\,\mathrm{NE}(0)\right)\sinh(\frac{k}{2}t) + \frac{NE(0)}{2}\cosh(\frac{k}{2}t)\right) & t \leq t_1 \\ b_{11}(t-t_1)NE(t_1) + b_{12}(t-t_1)RU(t_1) & t_1 < t < t_2 \\ \frac{2}{l+1}RU(t_2)e^{-kl(t-t_2)} + NE(t_2) - \frac{2}{l+1}RU(t_2) & t_2 \leq t < t_3 \end{cases} \tag{42}$$

$$RU(t) = \begin{cases} e^{-\frac{k}{2}(2l+1)t}\left(\left((2l+1)\,RU(0) + \frac{1}{4}\left(1-(2l+1)^2\right)NE(0)\right)\sinh(\frac{k}{2}t) + \mathrm{RU}(0)\cosh(\frac{k}{2}t)\right) & t \leq t_1 \\ b_{21}(t-t_1)NE(t_1) + b_{22}(t-t_1)RU(t_1) & t_1 < t < t_2 \\ RU(t_2)e^{-kl(t-t_2)} & t_2 \leq t < t_3 \end{cases} \tag{43}$$

$$N_P(t) = \begin{cases} 2l + 1 + \frac{\left(\left(\frac{1}{2}(2l+1)^2 + \frac{1}{2}\right)NE(0) - 2(2l+1)RU(0)\right)\sinh(\frac{k}{2}t) + (-(2l+1)NE(0) + 2RU(0))\cosh(\frac{k}{2}t)}{2\left(\left(2\mathrm{RU}(0) - \frac{1}{2}(2l+1)\mathrm{NE}(0)\right)\sinh(\frac{k}{2}t) + \frac{NE(0)}{2}\cosh(\frac{k}{2}t)\right)} & t \leq t_1 \\ \frac{2b_{21}(t-t_1)NE(t_1) + 2b_{22}(t-t_1)RU(t_1)}{b_{11}(t-t_1)NE(t_1) + b_{12}(t-t_1)RU(t_1)} & t_1 < t < t_2 \\ l + 1 & t_2 \leq t < t_3 \end{cases} \tag{44}$$

with $b_{11}(t)$, $b_{12}(t)$, $b_{21}(t)$ and $b_{22}(t)$ from equations (29) to (32) and $NE(t_1)$, $NE(t_2)$, $RU(t_1)$ and $RU(t_2)$ from the corresponding previous parts of the function.