Chapter 6

Polymerization and polymer size distribution

The purpose of this summary is to show how to arrive at the correct equation (6.6) for monomer depletion in a model for size distribution of polymers.

6.1 Polymerization Equations

We define $p_i(t)$ to be the (mean) number of polymers with i monomer subunits at time t. Think of setting up a large number of experimental replicates and measuring $p_i(t)$ for each, then averaging the data to see that p_i need not be an integer. We also let c be concentration of monomers.

Suppose the smallest polymer that can exist is made up of m monomer subunits. Then, by the Law of Mass Action, the rate of formation of that smallest size satisfies an equation of the form

$$\frac{dp_m}{dt} = k_{init}c^m - \gamma p_m - ck_f p_m + k_r p_{m+1}.$$

Here we have assumed initiation at some rate k_{init} and complete disassembly at rate γ. We also use the notation k_r for the reverse and k_f for the forward rates constants. For larger size classes, p_i we take

$$\frac{dp_i}{dt} = ck_f p_{i-1} - (ck_f + k_r)p_i + k_r p_{i+1}$$

About units, let us note that k_r, ck_f must have units of 1/time. The total number of polymer pieces is

$$N(t) = \sum_{i=m}^{\infty} p_i(t)$$

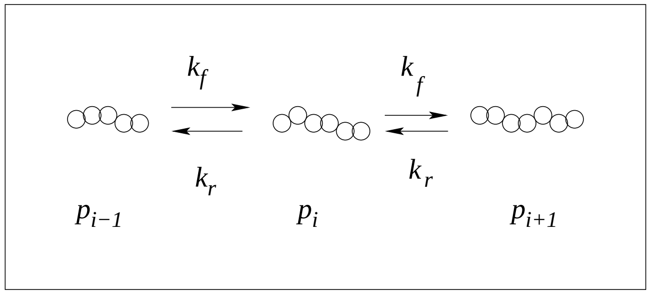

Figure 6.1: Keeping track of polymers of all sizes.

This is not necessarily constant, since new polymers can be nucleated from monomers. The total mass of the system is

$$M(t) = c(t) + \sum_{i=m}^{\infty} i p_i(t).$$

We take usually one of two scenarios: (i) The monomer pool is so large that it never gets depleted or (ii) The total mass M is constant. Here we consider scenario II.

6.2 Constant total mass

In this case, the mass (which consists of the sum of all free subunits plus those inside polymers) is:

$$M = c(t) + \sum_{i=m}^{\infty} i p_i(t) = \text{Constant}$$

Then constant mass means that

$$\frac{dM}{dt} = \frac{dc}{dt} + \sum_{i=m}^{\infty} i \frac{dp_i(t)}{dt} = 0$$

so in this case

$$\frac{dc}{dt} = -\sum_{i=m}^{\infty} i \frac{dp_i(t)}{dt}$$

We can arrive at the correct equation for monomers using mass conservation. Form the system of equations for the number of polymers in each size class.

6.2.1 Number of polymers of size i

$$\frac{dp_m}{dt} = k_{init}c^m - \gamma p_m - ck_f p_m + k_r p_{m+1}, \tag{6.1a}$$
$$\vdots$$
$$\frac{dp_{i-1}}{dt} = ck_f p_{i-2} - (ck_f + k_r)p_{i-1} + k_r p_i, \tag{6.1b}$$
$$\frac{dp_i}{dt} = ck_f p_{i-1} - (ck_f + k_r)p_i + k_r p_{i+1}, \tag{6.1c}$$
$$\frac{dp_{i+1}}{dt} = ck_f p_i - (ck_f + k_r)p_{i+1} + k_r p_{i+2}, \tag{6.1d}$$
$$\vdots$$

6.2.2 Mass of polymers of size i

The mass in size class i is $ip_i(t)$, since each polymer in that class has i monomers in it. From the above, we can get the equation for the *mass* in class i as follows:

$$i\frac{dp_i}{dt} = ick_f p_{i-1} - i(ck_f + k_r)p_i + ik_r p_{i+1}$$

We regroup terms and rewrite this as

$$i\frac{dp_i}{dt} = ick_f p_{i-1} - (i - 1 + 1)k_r p_i - (i + 1 - 1)ck_f p_i + ik_r p_{i+1}$$

or simply

$$i\frac{dp_i}{dt} = ick_f p_{i-1} - (i - 1)k_r p_i - (i + 1)ck_f p_i + ik_r p_{i+1} + [(ck_f - k_r)p_i]$$

Using this idea on each of the mass equations leads to a system that looks like

$$\begin{aligned}(i-1)\frac{dp_{i-1}}{dt} &= (i-1)ck_f p_{i-2} - (i-2)k_r p_{i-1} - ick_f p_{i-1} + (i-1)k_r p_i \\ &\quad + [(ck_f - k_r)p_{i-1}], \qquad (6.2a)\\ i\frac{dp_i}{dt} &= ick_f p_{i-1} - (i-1)k_r p_i - (i+1)ck_f p_i + ik_r p_{i+1} \\ &\quad + [(ck_f - k_r)p_i] \qquad (6.2b)\\ (i+1)\frac{dp_{i+1}}{dt} &= (i+1)ck_f p_i - ik_r p_{i+1} - (i+2)ck_f p_{i+1} + (i+1)k_r p_{i+2} \\ &\quad + [(ck_f - k_r)p_{i+1}] \qquad (6.2c)\end{aligned}$$

6.2.3 Simplifying the mass equations

Now observe that when we sum all these equations we get cancellations of terms shown in same color below

$$(i-1)\frac{dp_{i-1}}{dt} = (i-1)ck_f p_{i-2} - (i-2)k_r p_{i-1} - ick_f p_{i-1} + (i-1)k_r p_i + [(ck_f - k_r)p_{i-1}], \tag{6.3a}$$

$$i\frac{dp_i}{dt} = ick_f p_{i-1} - (i-1)k_r p_i - (i+1)ck_f p_i + ik_r p_{i+1} + [(ck_f - k_r)p_i] \tag{6.3b}$$

$$(i+1)\frac{dp_{i+1}}{dt} = (i+1)ck_f p_i - ik_r p_{i+1} - (i+2)ck_f p_{i+1} + (i+1)k_r p_{i+2} + [(ck_f - k_r)p_{i+1}] \tag{6.3c}$$

Analogous terms will cancel out with earlier or later equations when we sum the whole set, leaving only the terms $(ck_f - k_r)p_i$ from the ith equation for each $i = (m+1)\ldots$.

Using the same kind of idea for the smallest size class we get:

$$m\frac{dp_m}{dt} = mk_{init}c^m - (m\gamma + k_r)p_m - (m+1)ck_f p_m + mk_r p_{m+1} + [(ck_f - k_r)p_m] \tag{6.4}$$

Now here is the “entire system”, showing in blue which terms will drop out once the equations are added:

$$m\frac{dp_m}{dt} = mk_{init}c^m - (m\gamma + k_r)p_m - (m+1)ck_f p_m + mk_r p_{m+1} + [(ck_f - k_r)p_m] \qquad \vdots$$

$$(i-1)\frac{dp_{i-1}}{dt} = (i-1)ck_f p_{i-2} - (i-2)k_r p_{i-1} - ick_f p_{i-1} + (i-1)k_r p_i + [(ck_f - k_r)p_{i-1}], \tag{6.5a}$$

$$i\frac{dp_i}{dt} = ick_f p_{i-1} - (i-1)k_r p_i - (i+1)ck_f p_i + ik_r p_{i+1} + [(ck_f - k_r)p_i] \tag{6.5b}$$

$$(i+1)\frac{dp_{i+1}}{dt} = (i+1)ck_f p_i - ik_r p_{i+1} - (i+2)ck_f p_{i+1} + (i+1)k_r p_{i+2} + [(ck_f - k_r)p_{i+1}] \tag{6.5c}$$

6.2.4 Using mass balance to get the equation for monomers

When we add these up, we get the following:

$$\frac{d}{dt}\sum_{i=m}^{\infty} ip_i(t) = [mk_{init}c^m - (m\gamma + k_r)p_m] + \sum_{i=m}^{\infty}(ck_f - k_r)p_i$$

$$\frac{d}{dt}\sum_{i=m}^{\infty} ip_i(t) = [mk_{init}c^m - (m\gamma + k_r)p_m] + (ck_f - k_r)N(t)$$

Where we have used the number of pieces $N(t)$. Now by mass conservation, we get

$$\frac{dc}{dt} = -\left[mk_{init}c^m - (m\gamma + k_r)p_m\right] - (ck_f - k_r)N(t) \tag{6.6}$$

This completes the system and allows us to ensure we satisfy mass conservation.

Now we observe that in the early part of the process, starting with only monomers, $c(0) = M$, the first terms $mk_{init}c^m - (m\gamma + k_r)p_m$ will be most important, and in particular at the very beginning we expect to see

$$\frac{dc}{dt} \approx -mk_{init}c^m.$$

Much later, when there is less monomer, and fewer small polymers, we'd expect to see

$$\frac{dc}{dt} \approx -(ck_f - k_r)N(t).$$