EPFL

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

Step-Growth Polymerizations

1. The Carothers Equation

Step-growth polymerizations proceed via the covalent coupling of monomers with two (or sometimes more) complementary functional groups A and B. Typical organic chemistry base reactions, such as esterification, amidation, or urethane formation, are typically applied in this context. Most common is a reaction between two different bifunctional monomers A–A and B–B, each comprising two functional groups of type A and B, respectively. The difunctional nature of these monomers leads, first, to oligomeric species bearing unreacted A and B end groups that continue to react with one another in a stochastic manner, ultimately resulting in a polymer with a characteristic distribution of the molar mass.

The Carothers equation relates the number-average degree of polymerization with the conversion of functional groups and their stoichiometric ratio and allows to rationalize that high molecular weight polymers are only observed if the polymerization reaction is driven close to complete functional group conversion.

In a step-growth polymerization of bifunctional monomers A–A and B–B, the **stoichiometric ratio, r,** is the ratio between the initial number of A groups, $N_{\mathrm{A,0}}$, and B groups, $N_{\mathrm{B,0}}$. By convention, the A groups are defined to be the “limiting” type of groups, i.e., the type of groups that is present in lower amount, so that $r \leq 1$.

$$r = \frac{N_{\mathrm{A,0}}}{N_{\mathrm{B,0}}} \ . \tag{1}$$

Hence, the initial number of groups B can be expressed in terms of the initial number of groups A:

$$N_{\mathrm{B,0}} = \frac{N_{\mathrm{A,0}}}{r} \ . \tag{2}$$

As the molecular weight of a step-growth polymer continuously increases with every coupling reaction between functional groups, it is helpful to define the **conversion, p,** as the fraction of the functional groups A that has reacted (with functional groups B) at a given time t. The total number of functional A units present at time t, $N_{\mathrm{A,t}}$, can hence be expressed as

$$N_{\mathrm{A,t}} = N_{\mathrm{A,0}} - pN_{\mathrm{A,0}} = N_{\mathrm{A,0}}(1-p) \ , \tag{3}$$

where $N_{\mathrm{A,0}}$ is the initial amount of groups A at time $t = 0$. By definition, **each reacted functional group A must have exactly reacted with one functional group B**: if $pN_{\mathrm{A,0}}$ groups A have reacted, **the same** number $pN_{\mathrm{A,0}}$ of groups B must have reacted. The number of groups B at time t is therefore (the indices are not a mistake!):

$$N_{\mathrm{B,t}} = N_{\mathrm{B,0}} - pN_{\mathrm{A,0}} = N_{\mathrm{B,0}} - rpN_{\mathrm{B,0}} = N_{\mathrm{B,0}}(1 - rp) \ , \tag{4}$$

or, expressed in terms of groups A:

$$N_{\mathrm{B,t}} = N_{\mathrm{B,0}} - pN_{\mathrm{A,0}} = \frac{N_{\mathrm{A,0}}}{r} - pN_{\mathrm{A,0}} = N_{\mathrm{A,0}}\left(\frac{1}{r} - p\right) . \tag{5}$$

The total number of initially present monomer molecules, N_0, is given by the total number of functional groups divided by two, which accounts for the fact that the molecules are difunctional:

$$N_0 = \frac{N_{A,0} + N_{B,0}}{2} = \frac{N_{A,0}\left(1 + \frac{1}{r}\right)}{2} . \tag{6}$$

Each growing polymer chain has exactly two end groups of either group A or B. The total number of polymer chains, N, is therefore given by the sum of the total number of unreacted A and B groups **divided by two**, which can be expressed as a function of the respective starting amounts of A and B groups, $N_{\mathrm{A,0}}$ and $N_{\mathrm{B,0}}$:

$$N = \frac{N_A + N_B}{2} = \frac{N_{A,0}(1-p) + N_{B,0}(1-rp)}{2} = \frac{N_{A,0}(1-p) + \frac{N_{A,0}}{r}(1-rp)}{2} = \frac{N_{A,0}}{2}\left(1 - 2p + \frac{1}{r}\right) . \tag{7}$$

The number-average degree of polymerization, $\bar{X}_n$, which is the average number of repeat units per chain, can hence be calculated as the number of initially present molecules divided by the total number of present polymer chains, which results in the **general form of the Carothers equation**

$$\bar{X}_n = \frac{N_0}{N} = \frac{1 + r}{1 + r - 2rp} . \tag{8}$$

The Carothers equation can be simplified for two kinds of boundary conditions. On one side, for **perfectly stoichiometric conditions (r = 1)**, Equation 8 becomes

$$\bar{X}_n = \frac{1}{1 - p} . \tag{9}$$

In this case, the number-average degree of polymerization, $\bar{X}_n$ is a hyperbolic function of conversion p, meaning that **functional group conversions close to unity are required to obtain high-molecular weight polymers.** On the other side, even in the hypothetical case of **complete functional group conversion (p = 1)**, any **deviation from perfectly stoichiometric conditions** results in a significant reduction of the degree of polymerization:

$$\bar{X}_n = \frac{1 + r}{1 - r} . \tag{10}$$

Moreover, Equations 8 and 9 also imply that it is difficult to obtain linear polymers with high average molar masses by step growth polymerization in the laboratory, and even those obtained by industrial processes rarely exceed 100,000 g/mol, depending on the monomer.

2. Molar Mass Distribution in Step-Growth Polymerizations

In order to derive the "most probable" molar mass distribution for step-growth polymerizations (which is valid for both the polymerization of a stoichiometric A-A/B-B system and A-B-type monomers), an equal reactivity of the functional groups throughout the polymerization is usually assumed, that is, the reactivity of functional groups is independent on the molar mass of the growing polymer chain. For many step-growth polymerization this has indeed proven to be a reasonable assumption and allows one to perform some simple statistical considerations leading to an expression for the **Flory-Schulz molar mass distribution function**.

In a system initially containing N_0 difunctional monomers whose two functional groups can react with one another (assuming that ring formation is negligible), the probability that one such coupling reaction has occurred is then equivalent to the conversion p. The probability that a functional group has not reacted is, accordingly, $1 - p$. Thus, the probability that a given chain contains x monomers after a certain period of time, i. e., that $x - 1$ coupling reactions have taken place, and one functional group remains unreacted is given by the **number-distribution function**

$$P_x = p^{x-1}(1-p) \ . \tag{11}$$

The total number of chains in the system is

$$N = N_0(1-p) \ , \tag{12}$$

as there are N_0 molecules at the start. Each time one end of one of these molecules reacts, the total number of molecules decreases by 1. So, after $N_0\,p$ reactions, the number of remaining molecules is $N_0 - N_0\,p = N_0\,(1 - p)$. This relationship is also reflected by the Carothers equation (compare with Equations 8 and 9). The number of chains containing x repeat units is accordingly given by

$$N_x = NP_x = Np^{x-1}(1-p) = N_0 p^{x-1}(1-p)^2 \ . \tag{13}$$

The weight fraction w_x of the molecules containing x monomers is then given by the total mass m_x of molecules with a degree of polymerization x divided by the total mass of all molecules, which can also be expressed in terms of the molar mass of a repeat unit, M_0. The **weight-distribution function** can accordingly be expressed as

$$w_x = \frac{m_x}{\sum m_x} = \frac{N_x\,(x\,M_0)}{N_0\,M_0} = \frac{x\,N_x}{N_0} = x(1-p)^2 p^{x-1} \ , \tag{14}$$

which is usually referred to as the **most probable molar mass distribution function and is usually referred to as Flory-Schulz distribution** in polymer science. The number fraction (Equation 13) implies that, even in high molar mass polymers, shorter polymer chains remain favored over longer ones in terms of the number fraction, and the monomer dominates over any other chain length for any conversion. However, since the molar mass of monomers and shorter chains is lower than that of longer chains, the corresponding **weight fraction, w_x,** displays a maximum that shifts towards higher degrees of polymerization as the conversion increases, in line with the Carothers equation (Equation 9).

3. Molar Mass Averages and Dispersity

In order to derive an expression for the **number-average molar mass, $\bar{M}_n$,** defined as *the total sample weight over the total number of molecules*, one can start from the Flory-Schulz distribution

$$\bar{M}_n = \frac{\sum_{x=1}^{\infty} x\, N_x\, M_0}{\sum_{x=1}^{\infty} N_x} = M_0 \frac{\sum_{x=1}^{\infty} x\, N_0\, p^{x-1}\,(1-p)^2}{\sum_{x=1}^{\infty} N_0\, p^{x-1}\,(1-p)^2} = M_0 \frac{\sum_{x=1}^{\infty} x\, p^{x-1}}{\sum_{x=1}^{\infty} p^{x-1}} \ . \tag{15}$$

One can then apply Taylor series expansions that converge to known solutions for $p < 1$ (see Equations 20 to 22, Appendix), for simplifying both numerator and denominator of Equation 15:

$$\bar{M}_n = M_o \frac{\sum_{x=1}^{\infty} x\, p^{x-1}}{\sum_{x=1}^{\infty} p^{x-1}} = M_o \frac{\frac{d}{dp}\sum_{i=0}^{\infty} p^x}{(1-p)^{-1}} = M_o \frac{(1-p)^{-2}}{(1-p)^{-1}} = \frac{M_o}{1-p} \ . \tag{16}$$

One can find an analogous solution for the weight average molar mass, $\bar{M}_w$, starting from the Flory-Schulz distribution

$$\bar{M}_w = \frac{\sum_{x=1}^{\infty} N_x\, M_x^2}{\sum_{x=1}^{\infty} N_x\, M_x} = \frac{\sum_{x=1}^{\infty} N_x\, x^2\, M_0^2}{\sum_{x=1}^{\infty} N_x\, x\, M_0} = M_0 \frac{\sum_{x=1}^{\infty} N_0\, p^{x-1}\,(1-p)^2\, x^2}{\sum_{x=1}^{\infty} N_0\, p^{x-1}\,(1-p)^2\, x} = M_0 \frac{\sum_{x=1}^{\infty} p^{x-1}\, x^2}{\sum_{x=1}^{\infty} p^{x-1}\, x} \ . \tag{17}$$

Again applying Taylor series expansions that converge to known solutions for $p < 1$ (Equations 20, 22, and 23, Appendix), this results in :

$$\bar{M}_w = M_0 \frac{(1+p)(1-p)^{-3}}{(1-p)^{-2}} = M_0 \frac{1+p}{1-p} \ . \tag{18}$$

For the dispersity Đ, it therefore follows from Equation 16 and 18 that

$$Đ = \frac{\bar{M}_w}{\bar{M}_n} = 1 + p \ . \tag{19}$$

In conclusion, the Carothers equation shows that $\bar{M}_n$ and $\bar{M}_w$ become large only for a conversion approaching $p = 1$. At the same time, Equation 19 implies that the dispersity tends towards Đ = 2 within this limit, which is hence diagnostic of a well-behaved step growth polymerization.

Appendix

$$\sum_{x=0}^{\infty} y^{x} = 1 + y + y^{2} \ldots = \frac{1}{1-y} \tag{20}$$

$$\sum_{x=0}^{\infty} y^{x-1} = 1 + y + y^{2} \ldots + y^{x-1} = \frac{1}{y}\left(\sum_{i=0}^{\infty} y^{x} - 1\right) = \frac{1}{y}\left(\frac{1}{1-y} - 1\right) = \frac{1}{1-y} \tag{21}$$

$$\sum_{x=0}^{\infty} x y^{x-1} = \sum_{x=0}^{\infty} \frac{d}{dy} y^{x} = \frac{d}{dy} \sum_{x=0}^{\infty} y^{x} = \frac{d}{dy} \frac{1}{1-y} = \frac{1}{(1-y)^{2}} \tag{22}$$

$$\begin{aligned} \sum_{x=0}^{\infty} x^{2} y^{x-1} &= y \sum_{x=0}^{\infty} x^{2} y^{x-2} = y \sum_{x=0}^{\infty} y^{x-2} x(x-1) + y^{x-1} x = y \frac{d^{2}}{dy^{2}} \frac{1}{1-y} + \frac{d}{dy} \frac{1}{1-y} \\ &= \frac{2y}{(1-y)^{3}} + \frac{1}{(1-y)^{2}} = \frac{1+y}{(1-y)^{3}} \end{aligned} \tag{23}$$