Relationship between average functionality, extent of reaction and degree of polymerization:

W.H. Carothers derived a general expression, relating average functionality ($f$), extent of reaction ($p$, defined as the fraction of functional groups/monomers that have reacted at time $t$) and average degree of polymerization ($\bar{X}_n$, defined as equal to the total number of bifunctional units initially added, $N_0$, divided by the remaining number of molecules $N$ after time $t$), for polycondensation reactions carried out for a time period $t$. The expression is commonly known as Carothers’ Equation.

Let $N_0$ be the total number of reacting molecules initially present giving an average functionality for the system as $f$. The related functional groups (say, -OH and -COOH) are also considered to be present in stoichiometric equivalence. Let $N$ be the number of molecules present at time $t$ when the extent of reaction is $p$.

Then, number of molecules lost during the process over the time period $t$ is $(N_0 - N)$; for each molecule lost, the number of functional groups lost is 2 (one of each kind) and hence the total number of functional groups lost is $2(N_0 - N)$ against the initial total number of $N_0 f$ functional groups.

Hence, the extent of reaction, $p = \frac{2(N_0 - N)}{N_0 f}$

Or,

$$ p = \frac{2}{f} \left(1 - \frac{N}{N_0}\right) $$

The average degree of polymerization (or more precisely, the number-average degree of polymerization), $\bar{X}_n$ is defined as the average number of structural units per polymer molecule which can simply be expressed as:

$$ \bar{X}_n = \frac{N_0}{N} $$

Combining, we get,

$$ p = \frac{2}{f} \left(1 - \frac{1}{\bar{X}_n}\right) $$

This is known as Carothers’ Equation is very important for the understanding and control of the growth of polymers through polycondensation reactions.

The critical extent of reaction $p_c$ at the gel point (for $\bar{X}_n = \infty$) is given by:

$$ p = \frac{2}{f} $$

Gelation implies the formation of essentially infinitely large polymer networks in the reaction mixture.

It is important to note that for a polymerization system, $\bar{X}_n$ given by $\bar{X}_n = \frac{1}{1-p}$ is the number-average degree of polymerization of the reaction mixture (including even the unreacted monomers) and not just of the polymer that has been formed. For a polymer, however, there is a subtle difference between the number average degree of polymerization, $\bar{X}_n$, and the average degree of polymerization, $\overline{DP}_n$. The former quantity is given by the average number of structural units per polymer chain, the residue from each monomer in the polymer chain being termed a structural unit (or a monomer unit). On the other hand, $\overline{DP}_n$ is defined as the average number of repeating units per polymer chain. So, $\bar{X}_n$ is not necessarily equal to $\overline{DP}_n$. For example, for an
average polyester chain represented by \( \text{H-(-O-R-CO-)_{100}} \text{OH} \), both \( \bar{X}_n \) and \( \overline{DP}_n \) are equal to 100, while for an average chain represented by \( \text{H-(-O-R-OOC-R-CO-)_{100}} \text{OH} \), \( \bar{X}_n \) 200 and \( \overline{DP}_n \) 100.

**Carother’s equation for bifunctional systems:**

For a bifunctional system, \( f = 2 \), and Carother’s equation reduces to:

\[
p = \left(1 - \frac{1}{\bar{X}_n}\right)
\]

This implies that that for \( p = 1 \), \( \bar{X}_n = \infty \), which means that for complete reaction, the average degree of polymerization will be infinity; but short of complete reaction, the degree of polymerization is always a finite quantity. Polymer obtained in a bifunctional system is, under all practical situations, linear and hence soluble and fusible. The upper theoretical limit in the degree of polymerization is infinity and this can be attained only in the hypothetical condition of completion of reaction between the functional groups (\( p = 1 \)). For bifunctional systems, the equation can be rearranged to express \( \bar{X}_n \) as

\[
\bar{X}_n = \frac{1}{1 - p}
\]

For an essentially quantitative synthesis of polyamides, where \( p \) is 0.9999, the \( \bar{X}_n \) is approximately 10,000, the value calculated using this equation:

\[
\bar{X}_n = \frac{1}{1 - p} = \frac{1}{1 - 0.9999} = 10000
\]

Consider a reaction that can be driven to 90% completion which is a relative high yield and not easy to achieve in a bulk polymerization. Then the average degree of polymerization \( \bar{X}_n \) is \( 1 / (1-0.9) = 10 \). However, a decamer is to short to have useful mechanical properties. In general, the molecular weight has to be about two times the entanglement weight which equals about 15 to 100 repeat units, depending of the structure of the molecules. For example, to obtain a \( \bar{X}_n = 50 \), polymerization has to be carried out to 98% completion, \( \bar{X}_n = 1 / (1-0.98) = 50 \). Therefore, a relative high conversion is required to attain a high degree of polymerization.

If the mean molecular weight of the repeat unit in the polymer molecules is \( M_0 \), then the average molecular weight of the polymer system is expressed as:

\[
\overline{M}_n = M_0 \bar{X}_n = \frac{M_0}{1 - p}
\]

**Carother’s equation for polyfunctional systems:**

A typical polyfunctional system in condensation polymerization is exemplified by the reaction between phthalic anhydride or phthalic acid and glycerol, i.e. by allowing a bifunctional acid to react with a trihydric alcohol.

As discussed before, this system is characterized by an average functionality of 2.4.
For this system, Carother’s equation will assume the form:

\[ p = \frac{2}{2.4} \left(1 - \frac{1}{X_n}\right) \]

Three-dimensional step-reaction polymers are produced from the polymerization of reactants with more than two functional groups per molecule. The structures of these polymers are more complex than those of linear step-reaction polymers. Three-dimensional polymerization is complicated experimentally by the occurrence of gelation, or the formation of essentially infinitely large polymer networks in the reaction mixture. The sudden onset of gelation marks the division of the mixture into two parts: the gel, which is insoluble in all non-degrading solvents, and the sol, which remains soluble and can be extracted from the gel. As the polymerization proceeds beyond the gel point, the amount of gel increases at the expense of sol, and the mixture rapidly transforms from a viscous liquid to an elastic material of infinite viscosity. It is thus essential to stop the polymerization reaction before the onset of gelation. Carother’s reaction can help us in determining the critical extent of reaction, \( p_c \), at which gelation or cross-linking would commence, i.e., at which point \( X_n \) would first assume a value of infinity. In the given example, the calculated value of \( p_c \) will be \( 2/2.4 = 0.83 \).

Thus, it is clearly seen that at the point of a theoretical extent of reaction \( p = 0.83 \), i.e., when the reaction is 83% complete, the polymer being formed in the polycondensation system gets cross-linked and, hence, turns into an insoluble, infusible gelled mass. Technically, such a condensation polymerization cannot and should not be allowed to proceed beyond this point (83% completion), or otherwise the reaction mass would turn into an unusable product. In fact, it is advisable to arrest the reaction nearly 10–15% earlier in \( p \) to avoid damage of the reaction kettle and to collect a good quality product which would be useful and which could be easily manipulated in subsequent steps.

The usefulness of Carothers’ Equation lies in the linking of \( p, f \) and \( X_n \) in one expression, and in the fact that it can be used to predict gelation in polyfunctional systems. The limitation of the equation is that practically gelation starts even at earlier stages than predicted by the equation because of uncontrolled local conditions in the hot viscous reaction mass. Moreover, this equation is applicable to polycondensation reactions only, and it loses relevance in the context of addition or chain growth polymerization.

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