Number-Average Degree of Polymerization in Condensation Reactions

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NEW INTERPRETATIONS

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ABSTRACT

Number-average degree of polymerization in step-growth polymerizations can be estimated by several methods which yield consistent results if definition of the term "average functionality" is modified to suit the particular context. An example is given of a simple alkyd recipe.

Calculations of the number-average degree of polymerization, $\overline{X}_n$, as a function of extent of reaction are useful in designing and controlling condensation polymerizations which yield branched polymers. In the pioneering work of Carothers [1] the reaction mixture was assumed to gel when $\overline{X}_n$ became infinite. An infinite network forms when there is one cross-link per weight-average molecule [2, 3] and gel point calculations should therefore be based on $\overline{X}_w$ rather than $\overline{X}_n$. Such calculations are, however, only of limited use in the design of practical polymerization mixtures, despite numerous modifications of the basic concepts (Refs. 4-9,

for example). The major reasons for lack of agreement between
calculated and observed gel points probably include intramolecular
reactions, imperfect mixing, loss of functional groups through side
reactions, unequal reactivity of functional groups of the same type,
and the possibility that estimations correspond to initial formation
of three-dimensional polymer whereas most observations reflect
the presence of massive amounts of gel [10].

Because of these shortcomings, molecular weight calculations
are useful mainly for systematic modifications of formulations
which have unsatisfactory property balances rather than for accurate
predictions of gel points under practical operating conditions. Since
$\overline{X}_n$ estimates are more convenient and less complicated than $\overline{X}_w$ or
molecular weight distribution calculations for such purposes, the
design of branched condensation polymers still relies heavily on
the former parameter. The most widely used current methods for
estimation of $\overline{X}_n$ in such systems involve modified functionality
concepts related to Carother's original approach or to Flory's
statistical calculations [2]. The two systems seem to be regarded
as mutually exclusive, perhaps because both use the term "function-
ality" with somewhat different meanings. This note is intended to
show that these methods are equivalent both to each other when
average functionality is defined in context, and to a stoichiometric
calculation which avoids the use of this term entirely. As a general
example, $\overline{X}_n$ is calculated for a polyesterification reaction in which
the functionalities of the reactants differ and the acid and hydroxyl
groups are not present in equivalent concentrations.

Functionality of a monomer in this connection is defined as usual
as the number of positions in the molecule available for reaction
under the specified conditions. (A glycol is bifunctional in poly-
esterifications.) Carothers derived an expression linking $\overline{X}_n$,
extent of reaction, p, and average functionality, f_{AV}, for equal
concentrations of both types of functional groups involved in the
polymerization reaction (1). The average functionality is defined
in this case by

$$f_{AV} = \Sigma N_i f_i / \Sigma N_i \tag{1}$$

where N_i is the number of molecules of monomer i with functionality
f_i and the average is taken over all monomers in the reaction mixture.

$\Sigma N_i = N_o$ = the initial number of monomers, and N = the total number of monomer and polymer molecules when the reaction has proceeded to an extent p. Since one molecule and two different functional groups are lost every time a new linkage is formed, $2(N_o - N)$ functional groups are removed in forming $(N_o - N)$ linkages. By definition

$$p = 2(N_o - N)/N_o f_{AV} \tag{2}$$

where $N_o f_{AV}$ is the initial number of functional groups. Then

$$N = N_o - \frac{N_o p f_{AV}}{2} \tag{3}$$

Since $\overline{X}_n \equiv$ number of initial monomers/number of molecules remaining,

$$\overline{X}_n = \frac{N_o}{N} = \frac{2}{2 - p f_{AV}} \tag{4}$$

Here $\overline{X}_n$ is the number-average degree of polymerization of the mixture of polymer and monomer present when a fraction p of either or both functional group types has reacted. $\overline{X}_n$ refers to the total number of initial monomer units in a number-average molecule. It does not have the usual meaning of number of repeating units and its relation to the conventional definition will depend on whether A-B links are formed from reaction of A-A and B-B monomers or from A-B monomers. The definition of $\overline{X}_n$ used here is probably more realistic since the assignment of a repeating unit structure to highly branched polymers tends to be a vague exercise.

In nonstoichiometric mixtures the excess reactant does not enter the polymerization in the absence of side reactions and should not be counted in calculating f_{AV} [11]. Thus in a polymerization which forms A-B links, if $N_A < N_B$, then

$$f_{AV} = \frac{2N_A}{N_A + N_B} \tag{5}$$

$\overline{X}_n$ is still given by Eq. (4), but p is now the fractional conversion of the functional grouping in deficient concentration.

As an example, consider the simple alkyd recipe given in Table 1. Since there are only 4.2 acid equivalents, only this number of hydroxyl equivalents can react ideally. Assigning zero functionality to excess hydroxyl:

$$f_{AV} = \frac{\Sigma(\text{effective equivalents})}{\Sigma(\text{moles})} = \frac{4.2 + 4.2}{4.4} = 1.91 \tag{5a}$$

TABLE 1

Ingredient	Nominal functionality	Moles	Equivalents
Fatty acid	1	1.2	1.2
Phthalic anhydride	2	1.5	3.0
Glycerol	3	1.0	3.0
Glycol	2	0.7	1.4
		4.4	8.6

With this value of f_{AV} in Eq. (4), $\overline{X}_n$ is 7.2 at 90% conversion and 22 at 100% conversion of acid groups.

An alternative calculation involves use of a different average functionality with equations given initially by Flory [2]. For clarity, the derivation here is given explicitly for the alkyd system mentioned above. If n_1 and n_2 are the initial numbers of acid and hydroxyl groups, respectively, and $n_1 < n_2$, then

$$r = n_1/n_2 \tag{6}$$

where the ratio is always defined so that $0 < r < 1$. N_o, the total number of monomer units initially, is

$$N_o = \frac{n_1}{f_1'} + \frac{n_2}{f_2'} = n_1 \left[\frac{rf_2' + f_1'}{rf_2'f_1'} \right] \tag{7}$$

where f_1' and f_2' are average functionalities, respectively, of acid and hydroxyl monomers. In this case the average defined by Eq. (1) is not taken over the whole reaction mixture. For the example cited,

$$f_1' = \frac{(1.2 \times 1) + (1.5 \times 2)}{1.2 + 1.5} = 1.56$$

and

$$f_2' = \frac{(1.0 \times 3) + (0.7 \times 2)}{1.0 + 0.7} = 2.59$$

The extent of reaction, p, is based on the conversion of deficient monomer, as before, so that the number of acid groups remaining at this stage is $(n_1/f_1')(1 - p)$ and the number of linkages which have been formed is n_1p.

Neglecting the excess hydroxyl groups, the initial number of molecules in the mixture is $2n_1/f_1'$. The number of molecules remaining at p = initial number - number of molecules lost (or number of linkages formed) = $(2n_1/f_1') - n_1p$. The excess of hydroxy-containing monomers is

$$\frac{n_2}{f_2'} - \frac{n_1}{f_1'} = n_1 \left[\frac{f_1' - rf_2'}{rf_2'f_1'} \right]$$

Counting this excess, the total number of molecules, N, after conversion of a fraction p of the acid groups is

$$N = \frac{2n_1}{f_1'} - n_1p + n_1 \left[\frac{f_1' - rf_2'}{rf_2'f_1'} \right] \tag{8}$$

From Eqs. (7) and (8):

$$\bar{X}_n = \frac{N_o}{N} = \frac{rf_2' + f_1'}{rf_2' - rf_2'f_1'p + f_1'} \tag{9}$$

With the cited values of f_2' and f_1' and $r = (3.0 + 1.2)/3.0 + 1.4) = 0.955$,

$$\bar{X}_n = \frac{4.033}{4.033 - 3.859p} \tag{9a}$$

$\bar{X}_n$ is 7.2 at $p = 0.9$ and 23 at $p = 1$, with the difference from the preceding calculation due to rounding-off errors.

Stockmayer [3] has pointed out that $\bar{X}_n$ is always available from simple stoichiometry. No definitions of average functionality are involved if one proceeds as follows. At $p = 0.9$, 90% of the acid equivalents (the deficient concentration in this case) are consumed and an equivalent number of new linkages are formed. The number of molecules left in the system = original number - the number of linkages formed $= (1.2 + 1.5 + 1.0 + 0.7) - 0.9 (1.2 + 3.0) = 0.62 = N$. Since the number of structural units, N_o, is 4.4, $\bar{X}_n = 4.4/0.62 = 7.1$. Similarly, at $p = 1$, $N = 0.2$, and $\bar{X}_n = 4.4/0.2 = 22$, in agreement with the calculations based on average functionalities.

Author's Note

An article by French and Strecker [12] on ambiguities in the term functionality has come to my attention since the present manuscript was submitted. These authors use the symbol F to refer to number of chain ends united at branch points and f to refer to number of reactive groups per molecule. The applications of these two definitions of functionality are considered for estimates of gel point. The present article is concerned with the different practical definitions of f for calculating X_n. The two papers appear to be complementary. Each discusses variations in the term "functionality" which are not

covered by the other. Perhaps there are still other interpretations of this concept useful in similar or other calculations.

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