Polycondensations as Multiple Equilibria

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ABSTRACT

Multiple equilibrium theory is employed to derive equations
for the dependence of number-, mass-, and z-average degrees
of polymerization as function of equilibrium constant of self-
polycondensation and molar concentrations of monomer and
liberated compounds. The results are mathematically identical
with those of both probability and kinetic theory.

INTRODUCTION

Expressions for molar mass averages and molar mass distribu-
tions as function of conversion in equilibrium polycondensations have
been derived by Flory [1] in a most elegant manner using probability
theory. However, a certain uneasiness has always existed [2-6]
about the probability approach and thus about the correctness of the
results although kinetic derivations [2] and random walk statistics
[3] have been shown to lead to the same distribution functions. The
probability approach is also not easy to digest by students who never
had a formal training in probability theory.

Chemistry students are much more familiar with mass law action,
first used for polycondensation equilibria by Schulz [7]. He derived
for the number-average degree of polymerization the equation (1):

$$\langle X \rangle_n = 2\beta/[(4\beta + 1)^{1/2} - 1]$$

$$\simeq \beta^{1/2} \tag{1}$$

where $\beta = K/n_W$, K is the equilibrium constant, and n_W is the amount of liberated small molecules, e.g., water. The same equation is erroneously ascribed to Flory in a recent book [8]. Schulz's approach has been criticized for omission of terms in the derivation [6]. His expression for the degree of polymerization [see Eq. (1)] is obviously incorrect, because $\langle X \rangle_n$ and K have physical units of 1 and β the physical unit of an inverse amount (in mole). This paper, therefore, presents a treatment of polycondensation equilibria based on multiple equilibria. Multiple equilibrium theory has been previously employed for polymerization/depolymerization equilibria [9-12] and also for so-called open associations [13-16].
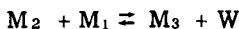
DERIVATIONS

The treatment demonstrated below applies to the selfcondensation of a monomer M_1 resulting in the formation of higher species M_2, M_3 etc. and the elimination of a compound W. An example may be the polycondensation of α,ω-hydroxyacids to polyesters under formation of water. Note that the derivations are based on the molar concentration of molecules and not on the molar concentrations of groups as in Flory's derivation. Otherwise, the same assumptions as in Flory's treatment are used: (1) equal thermodynamic chemical reactivity for all species of the system, (2) inclusion of monomer M_1 in the polymer and (3) assumption of unity activity coefficients for all species.

The equilibria to be considered are thus those shown in Eqs. (2).
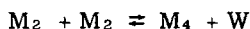
$2 M_1 \rightleftharpoons M_2 + W$

$$K = [M_2][W]/[M_1]^2$$

$M_2 + M_1 \rightleftharpoons M_3 + W$

$$K = [M_3][W]/[M_2][M_1] = [M_3][W]^2/K[M_1]^3$$

$M_3 + M_1 \rightleftharpoons M_4 + W$

$$K = [M_4][W]/[M_3][M_1] = [M_4][W]^3/K^2[M_1]^4$$

$$M_2 + M_2 \rightleftharpoons M_4 + W$$

$$K = [M_4][W]/[M_2]^2 = [M_4][W]^3/K^2[M_1]^4 \tag{2}$$

For convenience, a parameter Y is introduced and defined with the help of Eq. (1)

$$Y \equiv K[M_1]/[W]$$

$$= [M_i]/[M_{i-1}] \tag{3}$$

The following expressions can be easily defined and subsequently solved with Eqs. (2) and (3) if it is remembered that always $Y = [M_i]/[M_{i-1}] \leq 1$ [12]. The total molar concentration of polymer molecules is

$$[P] \equiv \sum_{i=1}^{\infty} [M_i] = [M_1] + [M_2] + [M_3] + \ldots$$

$$= [M_1]/(1 - Y) \tag{4}$$

The total concentration of monomeric units in the system is identical with the initial monomer concentration

$$[M_1]_0 = \sum_{i=1}^{\infty} X_i[M_i]$$

$$= [M_1] + 2[M_2] + 3[M_3] + \ldots.$$

$$= [M_1]/(1 - Y)^2 \tag{5}$$

Other sums of interest are

$$\sum_{i=1}^{\infty} X_i^2[M_i] = [M_1] + 4[M_2] + 9[M_3] + \ldots$$

$$= [M_1](1 + Y)/(1 - Y)^3 \tag{6}$$

$$\sum_{i=1}^{\infty} X_i^3 [M_i] = [M_1] + 8[M_2] + 27[M_3] + \ldots$$

$$= [M_1] (1 + 4Y + Y^2)/(1 - Y)^4 \tag{7}$$

These expressions can be combined to give the various average degrees of polymerization

$$\langle X \rangle_n \equiv \sum_{i=1}^{\infty} X_i [M_i] / \sum_{i=1}^{\infty} [M_i]$$

$$= 1/(1 - Y)$$

$$= 1/(1 - K[M_1][W]^{-1}$$

$$= [W]/([W] - K[M_1]) \tag{8}$$

$$\langle X \rangle_w \equiv \sum_{i=1}^{\infty} X_i^2 [M_i] / \sum_{i=1}^{\infty} X_i [M_i]$$

$$= (1 + Y)/(1 - Y)$$

$$= (1 + K[M_1][W]^{-1})/(1 - K[M_1][W]^{-1})$$

$$= ([W] + K[M_1])/([W] - K[M_1]) \tag{9}$$

$$\langle X \rangle_z \equiv \sum_{i=1}^{\infty} X_i^3 [M_i] / \sum_{i=1}^{\infty} X_i^2 [M_i]$$

$$= 1 + 4Y + Y^2 /(1 - Y)(1 + Y)$$

$$= \langle X \rangle_w + [(2Y/(1 - Y^2))] \tag{10}$$

Analog equations result if no compound W is released during the polycondensation; in this case, the factor [W] has to be substituted by 1 in Eqs. (8)-(10).

The monomer concentration [M₁] in equilibrium can be replaced by the initial monomer concentration in all these equations if Eqs. (5) and (8) are combined:

$$[M_1] = [M_1]_0 / \langle X \rangle_n^2 \tag{11}$$

whereas the equilibrium concentration of W is given by combining Eqs. (8) and (11)

$$[W] = K[M_1]_0 / \langle X \rangle_n (\langle X \rangle_n - 1) \tag{12}$$

The number-average degree of polymerization (and all other averages) can thus also be expressed in terms of the initial monomer concentration by resolving Eq. (12)

$$\langle X \rangle_n = \frac{1}{2} \pm \left(\frac{4 K[M_1]_0 + [W]}{4[W]} \right)^{1/2} \tag{13}$$

The equilibrium constants K for polyesterifications and polyamidations are normally in the order of 1-10. Initial neat monomer concentrations range somewhere in the order of 5 mole/kg. High degrees of polymerization can be thus achieved only if the equilibrium concentration of $[W]$ is very small. Furthermore, the sign in front of the square root has to be positive. Consequently, for high number-average degrees of polymerization

$$\langle X \rangle_n \simeq (K[M_1]_0 / [W])^{1/2} \tag{14}$$

The error Δ introduced by the approximation can be determined from Eqs. (12) and (14) as

$$\Delta = 1 - \{ [\langle X \rangle_n (\langle X \rangle_n - 1)]^{1/2} / \langle X \rangle_n \} \tag{15}$$

The error Δ is given in Table 1. It is lower than 1% at number-average degrees of polymerization greater than 50.

Equation (14) allows an estimate of the equilibrium concentration of W if the initial monomer concentration, the equilibrium constant, and the number average degree of polymerization are known. Setting $\langle X \rangle_n = 200$ (as usual for commercial products), $[M_1]_0 = 5$ mole/kg and $K = 8$, one receives $[W] = 10^{-3}$ mole/kg, or, with a molar mass of 100 g/mole for W, and $c_w = 10^{-4}$ g/g.

DISCUSSION

The expressions derived for the various average degrees of polymerization are mathematical identical with those given by Flory [1]:

TABLE 1. Comparison of Exact and Approximate Number-Average Degrees of Polymerization

$\langle X \rangle_n$		Error
Exact [Eq. (13)]	Approximate [Eq. (14)]	by Eq. (15) (%)
2	1.414	29.3
3	2.449	18.4
5	4.472	10.6
10	9.487	5.1
20	19.49	2.5
50	49.50	1.0

the conversion p of functional groups in his equations is replaced by the quantity $Y = K[M_1]/[W]$ in the multiple equilibrium approach. This quantity describes the conversion of monomer molecules at any given degree of reaction and is, according to Eq. (3), equal to the ratio of molar concentrations of any two adjacent polymer species. The good mathematical agreement between the expressions derived by probability and multiple equilibrium theory shows that the Flory probability theory is correct within the framework of assumptions.

The results can also be compared with those of kinetic derivations [6], which gave

$$\langle X \rangle_n = 1 + r \tag{16}$$

$$\langle X \rangle_w = 1 + 2r \tag{17}$$

where

$$r = k_1 \left(\sum_{i=1}^{\infty} [M_i] \right) / k_{-1}[W] \tag{18}$$

k_1 and k_{-1} are the rate constants for the forward and the backward reactions, respectively. The authors [6] did not give an explicit expression for the sum of the molar concentrations of all species. On setting $K = k_1/k_{-1}$ and inserting Eq. (4) into Eq. (17), r converts into

$$r = K[M_1]/([W] - K[M_1]) \tag{19}$$

which, upon introduction into Eqs. (16) and (17), leads to the same expressions as given in Eqs. (8) and (9). The kinetic approach thus gives the same results as the probability or the multiple equilibrium approach.

The probability approach describes the average degrees of polymerization as functions of a single parameter, the conversion p of functional groups. This is both an advantage and disadvantage, because p is not specific to the particular system under investigation. The multiple equilibrium approach, on the other hand, uses three parameters to describe the degrees of polymerization: equilibrium constant, equilibrium or initial monomer concentration, and equilibrium concentration of W. All these parameters can be determined experimentally: the average degrees of polymerization by absolute molar mass methods or sometimes by endgroup determination, the equilibrium monomer concentration by gel permeation chromatography or by extraction, the concentration of W in equilibrium by other suitable methods, e.g., by Karl-Fischer titration in the case of water, and the equilibrium constant by using monofunctional model compounds. By varying the initial monomer concentration and/or employing solvents with different solute/solvent interactions, internal checks on the validity of the underlying assumptions should be possible, e.g., on the influence of activity coefficients or on the variation of equilibrium constants with molar mass. Furthermore, the monomer concentration in equilibrium may be calculated directly from the initial monomer concentration and the number average degree of polymerization, if the investigated system follows the basic assumptions of the theory. This feature may be of interest as a rapid method for the determination of toxic, carcinogenic, or otherwise environmentally unsafe monomers.

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