Molecular Weight Distributions in Polycondensation

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SUMMARY

The distribution of molecular sizes for an equilibrium polycondensation process is derived kinetically. The expressions obtained for the system at equilibrium are formally the same as those derived by Flory. The expressions differ however, in that the i-mer concentration is shown to depend on both the polymer and by-product equilibrium concentrations.

INTRODUCTION

The distribution of molecular sizes in polycondensation has been derived by Flory [1]. Flory utilized probability theory to arrive at his result. Some of the steps taken in his derivation are not conceptually easy to follow [2]; indeed, it is said that Flory fortuitously arrived at the correct result due to the cancellation of two errors in his derivation [3]. An analysis of the distribution based on statistics for a random walk in one dimension [4] gives a result identical to that obtained by Flory.

A kinetic derivation of the distribution, based on an approach by Dostal and Raff [5], is given by Margerison and East [6]. Again, a result identical to that derived by Flory is obtained.

The derivations referred to above ignore the equilibrium nature of most polycondensation processes. Indeed, reasonable yields of polyamides, etc., can only be obtained on the removal of a by-product (in most cases water) from the reaction media. Since the polymers produced contain polar groups, removal of the last traces of water in the latter stages of the process may be impractical or even impossible. The effect of water on the distribution of the polymer produced is therefore of interest.

Schulz reported on a theoretical investigation of the effect of water on the distribution of the polymer produced in an equilibrium process [7]. The distribution derived is also similar to that obtained by Flory, and consequently the random distribution of molecular sizes is also called the Schulz-Flory distribution. One consequence of Schulz's [7] analysis is that water removal determines the rate of polymer production, a result dismissed by Flory [8].

A close study of Schulz's [7] reaction scheme shows that many terms are omitted. Augmentation of i-mer concentration as a result of hydrolysis of higher mers is ignored. The rate of reaction of water with i-mer is not proportional to the i-mer concentration, but to the hydrolyzable bond concentration of the i-mer.

We report here a theoretical investigation into the effect of by-product on the equilibrium position of the polycondensation and on the distribution of polymer sizes produced at equilibrium.

THEORETICAL DEVELOPMENT

The reaction between bifunctional monomers such as ω-hydroxy carboxylic acids is given as

$$H(ORCO)_iOH + H(ORCO)_jOH \underset{k_1}{\overset{k}{\rightleftharpoons}} H(ORCO)_{i+j}OH + H_2O \qquad (1)$$
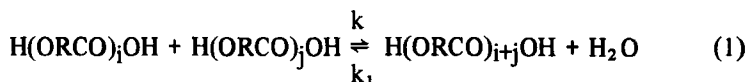
Both rate constants, k and k_1, are assumed independent of molecular size. Hydrolysis of the (i + j)mer does not necessarily lead to the original i and j-mers. The probability of producing the i-mer by hydrolysis of the (i + j)mer is 2/(i + j), since there are two hydrolyzable positions, i units from each end, which will lead to one i-mer.

If $[M_i]$ is the molar concentration of the i-mer

$$\frac{d[M_1]}{dt} = -2k[M][M_1] + 2k_1[H_2O]([M_2] + [M_3] + [M_4] + [M_5] + \ldots) \qquad (2)$$

where

$$[M] + \sum_{i=1} [M_i] \qquad (3)$$

$$\frac{d[M_2]}{dt} = k[M_1]^2 - 2k[M_2][M] - k_1[H_2O][M_2] + 2k_1[H_2O]([M_3] + [M_4]$$

$$+ [M_5] + [M_6] + \ldots) \qquad (4)$$

$$\frac{d[M_3]}{dt} = 2k[M_2][M_1] - 2k[M_3][M] - 2k_1[H_2O][M_3] +$$

$$2k_1[H_2O]([M_4] + [M_5] + [M_6] + [M_7] + \ldots) \qquad (5)$$

$$\frac{d[M_4]}{dt} = k[M_2]^2 + 2k[M_3][M_1] - 2k[M_4][M] - 3k_1[H_2O][M_4] +$$

$$2k_1[H_2O]([M_5] + [M_6] + [M_7] + \ldots) \qquad (6)$$

$$\frac{d[M]}{dt} = \frac{d[M_1]}{dt} + \frac{d[M_2]}{dt} + \frac{d[M_3]}{dt} + \frac{d[M_4]}{dt} + \ldots \qquad (7)$$

$$= k[M]^2 + k_1[H_2O] \sum_{i=1} i[M_{i+1}] = -k[M]^2 +$$

$$k_1[H_2O]([M_1]_0 - [M]) \qquad (8)$$

where $[M_1]_0$ is the initial monomer concentration.

At equilibrium

$$\frac{d[M]}{dt} = \frac{d[M_1]}{dt} = \frac{d[M_2]}{dt} = \frac{d[M_3]}{dt} = \ldots = \frac{d[M_i]}{dt} = \ldots = 0 \qquad (9)$$

for the monomer

$$2k[M_1][M] = 2k_1[H_2O]([M] - [M_1]) \qquad (10)$$

If we define

$$r = 1/y = k[M]/k_1[H_2O] \tag{11}$$

and insert the mole fraction of monomer, $x_1 = [M_1]/[M]$,

$$x_1 = 1/(1 + r) = y/(y + 1) \tag{12}$$

Similarly

$$x_2 = x_1(1 - x_1) = r/(1 + r)^2 = y/(y + 1)^2 \tag{13}$$

$$x_3 = x_1(1 - x_1)^2 = r^2/(1 + r)^3 = y/(y + 1)^3 \tag{14}$$

$$x_4 = x_1(1 - x_1)^3 = r^3/(1 + r)^4 = y/(y + 1)^4 \tag{15}$$

$$x_i = x_1(1 - x_1)^{i-1} = r^{i-1}/(1 + r)^i = y/(y + 1)^i \tag{16}$$

These expressions are formally the same as those derived by Flory [1]. According to Margerison and East [6]

$$x_1 = [M_1]/[M] = \frac{[M_1]_0}{(1 + k[M_1]_0 t)^2} \frac{1 + k[M_1]_0 t}{[M_1]_0} = \frac{1}{1 + k[M_1]_0 t} \tag{17}$$

where t is reaction time. The equations derived here for the distributions of sizes could be shown to be identical to Flory's expressions [1] if the equilibrium parameter r were shown to correspond to the quantity $k[M_1]_0 t$.

At equilibrium

$$k[M]^2 = k_1[H_2O]([M_1]_0 - [M]) \tag{18}$$

From Eqs. (11) and (18)

$$r = ([M_1]_0 - [M])/[M] \tag{19}$$

r thus equals the number of bonds per molecule.

In Margerison and East notation [6], after introducing the Flory [1] extent of reaction parameter, p,

$$\text{number of bonds per molecule} = \frac{[M_1]_0 p}{\text{number of molecules}} = \frac{[M_1]_0 k[M_1]_0 t}{1 + k[M_1]_0 t} \quad \frac{1 + k[M_1]_0 t}{[M_1]_0}$$

$$= k[M_1]_0 t \tag{20}$$

Hence we see that r and $k[M_1]_0 t$ have the same physical meaning, even though they occur in different derivations.

The relation between r and p is

$$\frac{x_{i+1}}{x_i} = p = \frac{r}{1+r} = \frac{1}{y+1} = \frac{k[M]}{k_1[H_2O] + k[M]} \tag{21}$$

Higher yields of polymer are obtained by removal of water from the reaction medium. However, p can never be 1 for real values of k_1 and nonzero values of $[H_2O]$. Where water causes hydrolysis of the polymer, it is impossible to have complete reaction as long as some water remains.

The number-average degree of polymerization is given as

$$\bar{x}_n \equiv \Sigma i\, x_i = \Sigma \frac{i\, r^{i-1}}{(r+1)^i} = \frac{1}{1+r} \Sigma i \left(\frac{r}{1+r}\right)^{i-1} \tag{22}$$

Introducing $a = (r/(1+r))$

$$\bar{x}_n = \frac{1}{1+r} \Sigma i a^{i-1} = \frac{1}{1+r} \frac{1}{(1-a)^2} = \frac{1}{1+r} \frac{1}{\left[1 - \left(\frac{r}{1+r}\right)\right]^2} = 1+r \tag{23}$$

This is equivalent to the Flory expression $\bar{x}_n = 1/(1-p)$.

The weight-average degree of polymerization is defined as

$$\bar{x}_w \equiv \frac{\Sigma i^2 x_i}{\Sigma i\, x_i} = \frac{\Sigma i^2 \dfrac{r^{i-1}}{(1+r)^i}}{\Sigma \dfrac{i r^{i-1}}{(1+r)^i}} = \frac{\dfrac{1}{1+r} \Sigma i^2 \left(\dfrac{r}{1+r}\right)^{i-1}}{\dfrac{1}{1+r} \Sigma i \left(\dfrac{r}{1+r}\right)^{i-1}} = \frac{\Sigma i^2 a^{i-1}}{\Sigma i\, a^{i-1}}$$

$$= \frac{\dfrac{1+a}{(1-a)^3}}{\dfrac{1}{(1-a)^2}} = \frac{1+\dfrac{r}{1+r}}{1-\dfrac{r}{1+r}} = 1+2r \tag{24}$$

This is equivalent to the Flory expression $\bar{x}_w = (1+p)/(1-p)$.

We see from Eq. (18) that removal of water increases the polymer yield at equilibrium. (The smaller the magnitude of [M], the larger the polymer yield.)

Also, from Eqs. (23) and (24), it is seen that water concentration influences the weight-average and number-average degrees of polymerization via the equilibrium parameter r.

Different molecular weight distributions, as distinguished by the ratio $\bar{x}_w/\bar{x}_n$, can also be produced by control of water concentration. However, these are only significantly different for small values of r (and hence small degrees of polymerization). Controlled distributions of high molecular weight material can, however, be produced if the monomer size is large, i.e., where the monomer is a polymer containing no hydrolyzable groups in the chain, but having functional groups at each end.

CONCLUSION

The molecular size distribution of polymers produced at equilibrium in an equilibrium polycondensation process has been shown to have the same form as one derived by Flory [1] for a polycondensation process where no back reaction is considered. The functions given here are in terms of a parameter r which is shown to have a clear physical significance at equilibrium (Eq. 19). Furthermore, the parameter is seen to have a definite relationship to Flory's probability p [1], although up till now it has not been unambiguously demonstrated that p can also have a physical significance for a system at equilibrium.

The kinetic scheme used above remains valid whether there is a by-product (in this case, water) involved or not, since its concentration is a constant at equilibrium. For example, processes where random scission and recombination of bonds occur, such as in the radiation of some polymer systems [9], can also be described by a reaction scheme of this type. Also, open association [10], where aggregation without limit proceeds with simultaneous dissociation of aggregates, can also be treated by a modified form of the presented scheme.

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