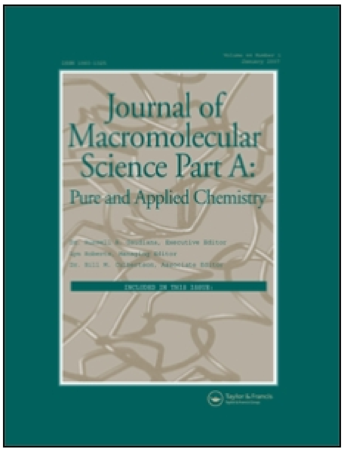

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Molecular Weight Distributions in Polymerization

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ABSTRACT

Molecular weight distributions corresponding to three separate termination kinetics are derived using an approximation which is valid for large degrees of polymerization. The derivation is straightforward and suitable for introducing students to the significance of kinetics on molecular weight distributions.

Although the determination of the molecular weight and number averages, and hence the standard deviation of the distribution, is not difficult and has been known for some time, the presentation in standard texts does not always present the essential features of these distributions in ways which are very clear to the average student. The derivation presented here is approximate but accurate for long chains, neglecting terms of the order of 1/(chain length).

We will discuss three cases of polymerization.

NO TERMINATION STEP: THE LIVING POLYMER

Polypeptide polymerization kinetics are assumed to be identical for each polymerization step.

Initiation: $p_1(0)$ is the concentration of the initiator which is provided initially, and it is assumed that at all times the total molar concentration of polymer is equal to the initial molar concentration of initiator

$$\sum_{\text{all } n} p_n(t) = p_1(0) \qquad t > 0 \tag{1}$$

Propagation:

$$M + P_n \xrightarrow{k_p} P_{n+1} \qquad \text{where } k_p \neq f(n) \tag{2}$$

A molar balance on M yields for the concentration, m, of monomer

$$\partial m/\partial t = -k_p m p_1(0) \tag{3}$$

Therefore

$$m = \exp[-k_p p_1(0)t]$$

A molar balance on the species P_n yields

$$\partial p_n/\partial t = k_p m(p_{n-1} - p_n) \tag{4}$$

If we assume that n is a continuous variable (even though we are only interested in certain integer values) we can expand p_n in a Taylor series

$$p_n = p_{n-1} + \frac{\partial p_n}{\partial n} + 0\left[\frac{\partial^2 p_n}{\partial n^2}\right] \tag{5}$$

then if we neglect the derivatives of order 2 or greater, we obtain

$$\frac{\partial p_n}{\partial t} = k_p \exp[-k_p p_1(0)t]\, \frac{\partial P_n}{\partial n} \tag{6}$$

The solution of this equation is by the method of characteristics which points out that since

$$dp = \frac{\partial p}{\partial t}\, dt + \frac{\partial p}{\partial n}\, dn \tag{7}$$

p is constant along the solution of the equation

$$dn/dt = k_p \exp[-k_p p_1(0)t] \qquad (8)$$

$$n(0) = 1$$

The distribution thus remains the same as the initial distribution (a delta function), and the ratio of the weight-average molecular weight to the number-average molecular weight is 1.

$$\overline{M}_n = \frac{\int j\delta(n)\,dj}{\int \delta(n)\,dj} = n\overline{M}_w = \frac{\int j^2\delta(n)\,dj}{\int j\delta(n)\,dj} \qquad (9)$$

where $\delta(n)$ is a delta function with the property

$$\int_0^\infty f(x)\,\delta(n)\,dx = f(n)$$

where n is defined by Eq. (8).

In other words, the polymerization proceeds with all the polymer present at any instant in time being of the same degree of polymerization. Since the ratio M_w/M_n is $1 + \sigma$ (the standard deviation of the distribution) in this case, the standard deviation is thus zero.

NOTE: Although the extreme sharpness of the distribution obtained immediately voids our major assumption stated after Eq. (5), nevertheless the conclusion that the distribution will be extremely sharp is valid since as soon as the distribution has broadened slightly the assumption becomes valid and a sharp distribution is thenceforward retained during the polymerization.

FREE RADICAL POLYMERIZATION

Termination by Disproportionation

The following kinetic scheme is assumed:

Initiation:

$$I \xrightarrow{k_i} P_1^0 \qquad (10)$$

Propagation:

$$M + P_n^0 \xrightarrow{k_p} P_{n+1}^0 \qquad (11)$$

Termination:

$$P_n^{\,0} + P_j^{\,0} \xrightarrow{k_t} P_n^{\,t} + P_j^{\,t} \qquad (12)$$

Again, making a molar balance on species $P_n^{\,0}$ of concentration $p_n^{\,0}$

$$\partial p_n^{\,0}/dt = mk_p(p_{n-1}^{0} - p_n^{\,0}) - \sum_{j=1}^{\infty} k_t p_n^{\,0} p_j^{\,0} \qquad (13)$$

Then making the steady-state approximation and also assuming that

$$p_n^{\,0} - p_{n-1}^{0} = \partial p^0/\partial n \qquad (14)$$

we obtain a continuous distribution equation which can be readily integrated if we assume a slow consumption of monomer

$$p_n^{\,0} = p_1^{\,0} \exp[-k_t \ell/k_p m]n \qquad \text{where } \ell = \sum_{j=1}^{\infty} p_j^{\,0} \qquad (15)$$

This is the distribution of the living polymer.

NOTE: Assumption (14) enables us to use continuous functions to describe the polymer distribution. Such functions are evaluated at integral values of n to obtain the discrete distributions.

The dead polymer is then formed by reaction of this living polymer with other living polymer.

$$p_n^{\,t} = k_t \ell p_1 \exp[-k_t \ell/k_p m]n \qquad (16)$$

where

$$p_1 = \frac{k_i}{k_p m}[I] \qquad (17)$$

and

$$\ell^2 = \frac{k_i}{k_t}[I] \quad \text{at pseudo steady state for the living polymer concentration} \qquad (18)$$

Therefore

$$p_n{}^t = \alpha e^{-\beta n}$$

where

$$\alpha^2 = \frac{(k_1[I])^3 k_t}{k_p{}^2 m^2} \tag{19}$$

$$\beta^2 = + \frac{k_i k_t [I]^2}{k_p M} = + \frac{k_i k_t [I]}{M^2 k_p{}^2} \tag{20}$$

Evaluation of the molecular weight averages are as follows

$$\overline{M}_n = \frac{\int_0^\infty n\alpha e^{-\beta n}\, dn}{\int_0^\infty \alpha e^{-\beta n}\, dn} \tag{21}$$

and after integrating by parts

$$\overline{M}_n = 1/\beta$$

similarly

$$\overline{M}_w = \frac{\int_0^\infty n^2 \alpha e^{-\beta n}\, dn}{\int_0^\infty \alpha n e^{-\beta n}\, dn} = \frac{2}{\beta} \tag{22}$$

Therefore

$$\overline{M}_w/\overline{M}_n = 2 \tag{23}$$

NOTE: Strictly, the integrals should be over the range $1 \leq n \leq \infty$ but the extended range is acceptable for large $\overline{M}_n$.

Termination by Combination

The following kinetic scheme is assumed

Initiation:

$$I \xrightarrow{k_i} P_1 \tag{24}$$

Propagation:

$$M + P_n^o \xrightarrow{k_p} P_{n+1}^o \qquad n \geq 1 \tag{25}$$

Termination:

$$P_n^o + P_j^o \xrightarrow{k_t} P_{n+j}^t \tag{26}$$

The balance on the living polymer is the same as in Case 2, but termination is given by the following expression since termination to give a chain of length n occurs by combination of any two living chains whose lengths sum to n.

$$P_n^t = k_t \sum_{j=1}^{n=1} P_{n-j}^o P_j^o \tag{27}$$

$$= k_t p_1^2 \sum_{j=1}^{n-1} \exp -\beta(n-j) \exp(-\beta_j) \tag{28}$$

$$= \gamma n \exp -\beta n \tag{29}$$

If

$$n \gg 1; \text{ and where } \gamma = k_t p_1^2 \tag{30}$$

The molecular weight distributions are then given by

$$\overline{M}_n = \frac{\gamma \int_0^\infty n^2 \exp(-\beta n)\, dn}{\gamma \int_0^\infty (n) \exp(-\beta n)\, dn} \tag{31}$$

and integrating by parts

$$\overline{M}_n = 2/\beta \tag{32}$$

Similarly

$$\overline{M}_w = \frac{\gamma \int_0^\infty n^3 \exp(-\beta n)\, dn}{\gamma \int_0^\infty n^2 \exp(-\beta n)\, dn} \tag{33}$$

and integrating by parts

$$\overline{M}_w = 3/\beta \tag{34}$$

Thus

$$\overline{M}_w/\overline{M}_n = 3/2 \text{ if } \beta \ll 1 \text{ (large molecular weights)} \tag{35}$$

We thus see how the breadth of the distribution changes for different polymerization kinetics.

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