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Relative and Absolute Measures of Heterogeneity of Polymer Sizes

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NEW INTERPRETATIONS

Relative and Absolute Measures of Heterogeneity of Polymer Sizes

INTRODUCTION

The common measure of relative heterogeneity of a polymer sample is the ratio M_w/M_n, where M_w is the weight-average molecular weight and M_n is the number-average molecular weight [1]. A convenient measure of the absolute heterogeneity of polymer sizes is the variance of the molecular weight distribution. The variance [Var(M)] is formulated in terms of M_w and M_n as follows:

$$\mathrm{Var}(M) \equiv E(M^2) - [E(M)]^2 \qquad (1)$$

where E(M) and $E(M^2)$ are, respectively, the first and second moments of the polymer molecular weight distribution taken about the origin. The rth moment of the molecular weight distribution about the origin is defined as

$$E(M^r) \equiv \sum_{i=1}^{\infty} (M_i)^r p(M_i) \qquad (2)$$

where M_i represents the molecular weight of polymer containing i units and $p(M_i)$ represents the fraction of polymer molecules with molecular weight M_i. It is easy to show that M_w and M_n can be represented in terms of moments as follows [1,2]:

$$M_n = E(M) \qquad (3)$$

$$M_w = E(M^2)/E(M) \qquad (4)$$

Substitution of $E(M^2)$ and E(M) in terms of M_w and M_n into Eq. (1) yields

$$\mathrm{Var}(M) = M_w M_n - (M_n)^2 \qquad (5)$$

The positive square root of the variance is defined as the standard deviation, σ:

$$\sigma = \sqrt{M_w M_n - (M_n)^2} \qquad (6)$$

The relative utilities of M_w/M_n and σ as measures of breadth of the molecular weight distribution will be illustrated for the Poisson distribution. The concentration distribution for species produced in a living polymerization described by a single rate constant with monomer concentration not held constant is given by [3]

$$P_n(\nu) = P_1^0 (\nu)^{n-1} e^{-\nu}/(n-1)! \tag{7}$$

and, for second-order disappearance of monomer,

$$\nu = -\frac{M^0}{P_1^0} e^{-kP_1^0 t} + \frac{M^0}{P_1^0} \tag{8}$$

where M^0 and P_1^0 represent initial concentrations of monomer and initiator, respectively, k is the rate constant, and t is time.

CALCULATION OF MOMENTS

$$E(M) = M \sum_{n=1}^{\infty} (n) \frac{(\nu)^{n-1} e^{-\nu}}{(n-1)!} \tag{9a}$$

where M is the molecular weight of a monomer unit.

$$E(M) = M(\nu + 1) \tag{9b}$$

$$E(M^2) = (M^2) \sum_{n=1}^{\infty} n^2 \frac{\nu^{n-1} e^{-\nu}}{(n-1)!} \tag{10a}$$

This sum is broken into three terms:

$$E(M^2) = (M)^2 \left[\sum_{n=1}^{\infty} (n-1)^2 \frac{\nu^{n-1} e^{-\nu}}{(n-1)!} + 2 \sum_{n=1}^{\infty} \frac{n\nu^{n-1} e^{-\nu}}{(n-1)!} - 1 \right] \tag{10b}$$

Evaluation of the summations yields

$$E(M^2) = (M)^2 (\nu^2 + 3\nu + 1) \tag{10c}$$

$$\mathrm{Var}(M) = (M)^2 \nu \tag{11a}$$

$$\sigma = M\sqrt{\nu} \tag{11b}$$

The ratio M_w/M_n is obtained by dividing Eq. (4) by Eq. (3):

$$\frac{M_w}{M_n} = 1 + \frac{\nu}{(\nu + 1)^2} \tag{12}$$

As the time of polymerization increases, the value of ν increases, reaching a limiting value of M^0/P_1^0 as $t \to \infty$. If, for example, $M^0/P_1^0 = 100$, then

$$\lim_{t \to \infty} (M_w/M_n) = 1.01 \tag{13}$$

The theoretical lowest limit of M_w/M_n can never be experimentally achieved, owing to spurious impurities causing termination and inability to obtain infinitely good mixing.

Consider now the variance. Since ν increases with time of polymerization, the variance also increases and reaches a maximum as time approaches infinity.

Two sample calculations are provided. Assume that $M = 44$ g/mole (molecular weight of ethylene oxide).

Case 1. At $\nu = 100$, $M_n = 4444$. From Eq. (12), $M_w/M_n = 1.01$. From Eq. (11b), $\sigma = M\sqrt{100} = 440$. Thus $\sigma/M_n = 0.099$. The absolute breadth of the molecular weight distribution could be described as 4444 ± 440, indicating that about two-thirds of the molecules have molecular weights between 4000 and 4880.

Case 2. At $\nu = 1000$, $M_n = 44,044$ and $M_w/M_n = 1.001$, $\sigma = 1470$. Thus $\sigma/M_n = 0.033$. The absolute breadth for this case is 44, 044 ± 1470.

The two sample calculations have shown that the absolute heterogeneity of molecular weights (measured by σ) increases as the number-average molecular weight of the polymer increases. However, the relative heterogeneity (measured by M_w/M_n or σ/M_n) decreases under these conditions. Figure 2 in [3] also illustrates this important point.

We conclude that investigators should consider reporting both M_w/M_n and σ for polymer samples.

COMMENT ON THE USE OF MOMENTS IN POLYMERIZATION KINETICS

The motivations for presenting the various molecular weight averages and their ratios as the appropriate ratios of the moments of the molecular weight distribution stems also from the theory of polymerization kinetics. In analyzing the kinetics of somewhat complex mechanisms, occasions arise when one can obtain the molecular weight distribution in the transformed expression by the method of Z transform (or generating function) but cannot invert the transform F(Z, t) to obtain the $P_n(t)$ [4]. Fortunately, the moments can be obtained rather easily as follows [5]:

$$E(M) = \left.\frac{\partial F(Z, t)}{\partial Z}\right]_{Z=1} \tag{14}$$

$$E(M^2) = \left.\frac{\partial^2 F(Z,t)}{\partial Z^2}\right]_{Z=1} + \left.\frac{\partial F(Z,t)}{\partial Z}\right]_{Z=1} \qquad (15)$$

Given E(M) and $E(M^2)$ from Eqs. (14) and (15), the values of M_w and M_n can be calculated from Eqs. (3) and (4).

This method of calculating M_n and M_w as a function of time is useful even when the expression for $P_n(t)$ is available, since obtaining E(M) and $E(M^2)$ by differentiation of the F(Z, t) is invariably easier than by evaluating the appropriate summations for E(M) and $E(M^2)$ using the $P_n(t)$ [cf. Eqs. (2), (9a), and (10a)].

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