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New Interpretations: Molecular Weight Averages for a Polymer

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ABSTRACT

The statement is often made in the polymer literature, without proof, that $\bar{M}_z \geq \bar{M}_w \geq \bar{M}_n$, where \bar{M}_z , \bar{M}_w , and \bar{M}_n are the z-, weight-, and number-average molecular weights respectively. Four proofs of a generalization of these inequalities are given. It is shown that a higher-order molecular weight average is larger than a lower-order one, regardless of the form of the molecular weight distributions, except for the case when all the molecules have the same molecular weight. A brief discussion of the viscosity-average molecular weight is also included.

INTRODUCTION

It is widely recognized [1a] that the weight-average molecular weight \bar{M}_w of a polymer is always larger than the number-average molecular weight \bar{M}_n , and the z-average molecular weight \bar{M}_z is in turn larger than \bar{M}_w , and so on. For justification, appeal is often made to numerical examples for specific simple distributions. Sometimes, appeal is made to the intuition, for example, that \bar{M}_w is larger than \bar{M}_n since high molecular weight portions of a molecular weight distribution get more weighting in calculating \bar{M}_w than in \bar{M}_n . Rarely does the proof appear in polymer texts, despite its fundamental importance in polymer science. (The work by Fujita [2] is the only such book in which we saw such a proof.)

In this article, we present four different proofs that a higher-order molecular weight average is larger than a lower-order average. Which of the derivations would be most suitable for a given student would depend on his mathematical background. The strict inequality holds for any molecular weight distribution except for the trivial case when all the molecules in the polymer have the same molecular mass. In the latter case, there is no need for averaging, and all the molecular weight averages are equal to each other.

K-TH-ORDER AVERAGE MOLECULAR WEIGHT

The k-th-order average molecular weight $\langle M \rangle_k$ of a polymer may be defined by the relation

$$\langle M \rangle_k = \frac{\sum_i M_i^k N_i}{\sum_i M_i^{k-1} N_i} \quad k = 1, 2, \dots \quad (1)$$

where N_i is the number of molecules (or moles) of the i-th molecular weight species whose molecular weight is M_i and m is the total number of different molecular weight species. To simplify the notation all summations \sum_i and \sum_j in this communication, it may be assumed, extend over all values of the index i or j , unless otherwise indicated.

Low-order average molecular weights have special names and

symbols: $\langle M \rangle_1 = \overline{M}_n$, $\langle M \rangle_2 = \overline{M}_w$, $\langle M \rangle_3 = \overline{M}_z$, etc. The inequality to be proved is

$$\langle M \rangle_{k+1} \geq \langle M \rangle_k \quad k = 1, 2, \dots \quad (2)$$

It is readily seen that a special case of Eq. (2) is the oft-quoted ordering:

$$M_n \leq M_w \leq M_z$$

The strict inequality holds if there are two or more molecular weight species ($m \geq 2$), and the equality holds in the trivial case of only one fraction ($m = 1$).

Proof A

Perhaps the shortest proof of relation (2) is made through the use of the Cauchy-Schwarz inequality [3, 4].

$$(\sum_i a_i^2) (\sum_i b_i^2) \geq (\sum_i a_i b_i)^2 \quad (3)$$

which is valid for any real values of a_i and b_i . If the substitutions

$$\begin{aligned} a_i &= (M_i^{k+1} N_i)^{1/2} \\ b_i &= (M_i^{k-1} N_i)^{1/2} \end{aligned} \quad (4)$$

are made into Eq. (3), one obtains

$$(\sum_i M_i^{k+1} N_i) (\sum_i M_i^{k-1} N_i) \geq (\sum_i M_i^k N_i)^2 \quad (5)$$

Since each sum in Eq. (5) is positive, it may be rearranged to give

$$\sum_i M_i^{k+1} N_i / \sum_i M_i^k N_i \geq \sum_i M_i^k N_i / \sum_i M_i^{k-1} N_i \quad (6)$$

which, in view of the definition (1) proves relation (2).

The equality sign in the Cauchy-Schwarz inequality holds only if $a_i = cb_i$ ($i = 1, 2, \dots, m$) where c is a constant [4]. With the a_i and b_i given by Eq. (4), this condition reads $c = M_i$ and c cannot be a constant except when there is only one species ($m = 1$).

Proof B

Perhaps, the most direct proof of relation (2), requiring only differential calculus, is made by showing that the first derivative of $\langle M \rangle_k$ with respect to k is positive. Here, we regard k as a continuous variable temporarily and also assume that $m \geq 2$. Differentiation of Eq. (1) yields:

$$d\langle M \rangle_k / dk = \frac{\sum_i \sum_j A_{ij}}{(\sum_i M_i^{k-1} N_i)^2} \quad (7)$$

where

$$A_{ij} = (M_i^{k-1} N_i M_j^{k-1} N_j) M_i \ln (M_i / M_j) \quad (8)$$

The double sum of A_{ij} , which occurs in the numerator of Eq. (7), may be rewritten as

$$\sum_{i=1}^m \sum_{j=1}^m A_{ij} = \sum_{i=1}^{j-1} \sum_{j=2}^m (A_{ij} + A_{ji}) \quad (9)$$

noting that $A_{ii} = 0$. Now, from Eq. (8) it is seen that

$$A_{ij} + A_{ji} = M_i^{k-1} N_i M_j^{k-1} N_j (M_i - M_j) \ln (M_i / M_j) \quad (10)$$

Since $M_i \neq M_j$, we have, for any combination of M_i and M_j ,

$$(M_i - M_j) \ln (M_i / M_j) > 0 \quad (11)$$

(It is interesting to note that Eq. (11) is the inequality used in

deriving Boltzmann's H-theorem [5, 6].) Now, returning to Eq. (7), we see that we have just shown that the numerator on the right-hand side is positive. Since the denominator is also clearly positive, we have

$$d\langle M \rangle_k / dk > 0 \quad (12)$$

which indicates that $\langle M \rangle_k$ is a monotonically increasing function of k when $m \geq 2$ in Eq. (1) and therefore relation (2) is proved (even in the case when k is not limited to integral values).

Proof C

This is probably the most elementary of the four proofs. First, we define

$$q_i^{(k-1)} = M_i^{k-1} N_i / \sum_i M_i^{k-1} N_i \quad k = 1, 2, \dots \quad (13)$$

and note that $q_i^{(k-1)}$ thus introduced is positive and satisfies the normalization condition:

$$\sum_i q_i^{(k-1)} = 1 \quad (14)$$

For $k = 1$, we have $q_i^{(0)}$, which is a normalized number (or molar) distribution of the molecular weight, and for $k = 2$, we have $q_i^{(1)}$ which is a normalized weight (or mass) distribution of the molecular weight.

Now $\langle M \rangle_k$ and $\langle M \rangle_{k+1}$ may be written in terms of $q_i^{(k-1)}$ as follows:

$$\begin{aligned} \langle M \rangle_k &= \sum_i M_i q_i \\ \langle M \rangle_{k+1} &= \sum_i M_i^2 q_i / \sum_i M_i q_i \end{aligned} \quad (15)$$

where we have dropped the superscript $(k-1)$ from q_i for simplicity. The variance of q_i is positive, i.e.,

$$\sum_i (M_i - \sum_j M_j q_j)^2 q_i \geq 0 \quad (16)$$

which may be rewritten as

$$\sum_i M_i^2 q_i \geq (\sum_i M_i q_i)^2 \quad (17)$$

Dividing both sides by $\sum_i M_i q_i$ (> 0), we obtain

$$\sum_i M_i^2 q_i / \sum_i M_i q_i \geq \sum_i M_i q_i \quad (18)$$

In view of Eqs. (15), this is equivalent to relation (2).

VISCOSITY-AVERAGE MOLECULAR WEIGHT

For polymers, there is another class of molecular weight averages called the viscosity-average molecular weight μ_a [7]. This is defined by

$$\mu_a = (\sum_i M_i^{1+a} N_i / \sum_i M_i N_i)^{1/a} \quad (19)$$

where a is the exponent appearing in the Mark-Houwink relation for the limiting viscosity number or intrinsic viscosity of polymer chains in solution. The value of a depends on the polymer, the solvent, and the temperature. It usually falls between 0.5 and 1.0 for uncharged flexible polymer chains. For polyelectrolytes in the absence of supporting electrolytes, it may come close to 2, which is also the value approached in the case of rigid rod-shaped macromolecules [1b].

The viscosity-average molecular weight μ_a defined by Eq. (19) is a generalized mean molecular weight of order a with $q_i^{(1)}$ = $M_i N_i / \sum_i M_i N_i$ used as the weighting function [4, 8, 9]. The generalized mean μ_a is a monotonically increasing function of a , and we have

$$M_1 \leq \mu_a \leq M_m \quad (20)$$

and

$$\lim_{a \rightarrow -\infty} \mu_a = M_1$$

$$\lim_{a \rightarrow \infty} \mu_a = M_m \quad (21)$$

where M_1 and M_m are the smallest and the largest molecular weights in the polymer.

As is well recognized [1, 9] μ_a and $\langle M \rangle_k$ coincide with each other at least at two points:

$$\mu_{-1} = \langle M \rangle_1 = M_n$$

$$\mu_1 = \langle M \rangle_2 = M_w \quad (22)$$

which can easily be seen by substituting $a = -1$ and $a = 1$ into Eq. (19) and comparing them with Eq. (1). We also note that the generalized mean becomes the root mean square for $a = 2$, the square mean root for $a = 1/2$. It approaches the geometric mean as a approaches zero [4, 8].

Proof D

In the preceding section, we have noted that with the weighting function $q_i^{(1)}$, we have $\mu_1 = \langle M \rangle_2$ and $\mu_{-1} = \langle M \rangle_1$. Since the generalized mean μ_a is a monotonically increasing function of a for any distribution, we have $\langle M \rangle_2 \geq \langle M \rangle_1$ immediately [9]. If we take the generalized mean molecular weight of order $+1$ and -1 with $q_i^{(k)}$ of Eq. (13) as the weighting function we get

$$\mu_1 = \langle M \rangle_{k+1}$$

$$\mu_{-1} = \langle M \rangle_k \quad k = 1, 2, \dots \quad (23)$$

Since $\mu_1 \geq \mu_{-1}$ for any distribution, we have Eq. (2) again.

CONCLUDING REMARKS

In the above, we have used discrete molecular weight distribution functions. It is often more convenient to use a continuous distribution function which is a good approximation to the inherently discrete molecular weight distribution of a polymer. We omit, however, the proofs of relation (2) in terms of the continuous molecular weight distribution function since they closely parallel the proofs using the discrete distribution function.

In summary, we note the following for any nontrivial ($m \geq 2$) molecular weight distribution: (a) the k -th-order average molecular weight $\langle M \rangle_k$ is defined for positive k and $\langle M \rangle_k$ increases as k increases; (b) the viscosity-average molecular weight μ_a is defined for a limited but continuous range of a and μ_a increases as a becomes larger; (c) $\langle M \rangle_k$ and μ_a coincide at least at two points: $\mu_{-1} = \langle M \rangle_1$ and $\mu_1 = \langle M \rangle_2$, if the range of a is extended.

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