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Exemplification of Homo-Polymer Average Chain Length and Weight Properties

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Abstract

In this short communication, two methods were shown for evaluating the homo-polymer number-average molecular weight (MWN), weight-average molecular weight (MWW), and poly dispersity index (PDI). The goal is to exemplify the cumbersome mathematical portray which heavily relies on the zeroth, first, and second moment frequency distribution of homo-polymer chains in a typical chain reaction and transform the portray into a more simplified version that simply relies on statistical parameters, namely, the mean and variance of a sample.

Keywords： Number Average Molecular Weight; Weight Average Molecular Weight; Polymer; Polymerization; Exemplification; Poly Dispersity Index; Chemical Engineering Education

Introduction

Chemical engineering realm more or less deals with naturally occurring phenomena or human-made processes where all obey basic natural laws as in chemical reaction engineering. The duty of a Chemical Engineering educator at the same time is to present and represent a phenomenon of interest in a context such that it is easy for the student to understand, without really compromising the premises of the phenomenon itself (i.e., the fundamental law or the set of fundamental laws, which governs the phenomenon of interest). Therefore, it is so important for a Chemical Engineering educator to simplify and exemplify the concept prior to entering the world of cumbersome equations (differential, algebraic, or both).

This can be done via drawing an analogy between the phenomenon under study and a social phenomenon, habit, or event that can be easily grabbed by the student. From my humble experience in teaching chemical engineering courses for naïve starting chemical engineering students, I found that it is imperative that the faculty member ought to simplify and exemplify the hard to understand concepts embodying the phenomenon of interest.

In the first example, I explained the physics behind models underlying mass transfer in both gas and liquid world [1]. In the second example, I demonstrated where to draw the demarcation line between a finite and semi-infinite medium and the applications of the latter in real chemical engineering life [2]. In this short communication, I will exemplify the notion behind the number and weight average molecular weight of a polymer, using simple statistical parameters.

The Homo-Polymer Properties in terms of Moments (Cumbersome Mathematics; the Moment Portray)

The average properties can be calculated as ratios of the moments. For a typical chain polymerization reaction which produces a homo-polymer, the <u>number average degree of polymerization</u> (<u>DPN</u>) is the ratio of the first to the zeroth moment, λ_1/λ_0. On the other hand, the <u>Weight or Volume average degree of polymerization</u> (<u>DPW</u>) is the ratio of the second to the first moment, λ_2/λ_1. Moments-based approach of calculating homo polymer properties can be found in [3, 4, 5].

In general, for a polymer with a chain length distribution, the moment frequency distribution is given by:

$$\lambda_m = \sum_{n=1}^{N} n^m Q_n \quad (1)$$

Where:

λ = Moment

m = Moment order

n = Chain length or degree of polymerization

Q_n = Number of moles of polymer of length n

The polymer average chain length and weight properties are then calculated as the following:

DPN = Number-average degree of polymerization = λ_1/λ_0=FMOM/ZMOM (2)

DPW = Weight-average degree of polymerization = λ_2/λ_1=SMOM/FMOM (3)

PDI = Poly Dispersity Index= DPW/DPN = (λ_2/λ_1) / (λ_1/λ_0)= $(\lambda_2 \times \lambda_0)/(\lambda_1)^2$ = (SMOM×ZMOM)/(FMOM)^2 (4)

MWN=Number-average molecular weight = DPN $\times \overline{\mathrm{M}}_{\mathrm{segment}}$ (5)

MWW=Weight-average molecular weight $=$ DPW $\times \overline{\mathrm{M}}_{\mathrm{segment}}$ (6)

I know ahead that the brain-average user will find it difficult to grasp or grab such terms. Therefore, I will explain the terminology based on a simple statistical approach.

The Homo-Polymer Properties in terms of the Mean and Variance (Simple Statistics; the Madonna Portray)

Let us consider that we have 100 monomeric units of C_3H_6. Let us say the homo-polymerization reaction (i.e., formation of polypropylene polymer) is initiated via different catalyst sites. The 100 building blocks can be put in so many different ways (i.e., configurations), depending on the rate constant of each type of active site. For the sake of clarifying the afore-mentioned definitions, we will consider the following cases:

The First Case: All 100 blocks (i.e. monomers) are put in one single polymer chain.

The Second Case: Two polymer chains each with 50 blocks.

The Third Case: Two polymer chains but one with 60 and another with 40 blocks.

The Fourth Case: Four polymer chains where the first has 10, the second 20, the third 30, and the fourth 40 blocks, adding up to 100 blocks.

Let us calculate the mean and variance for each case.

The First Case:

$$MWN = 100 \times M_o = 100M_o \quad (7)$$

$$\bar{X} = 100M_o \quad (8)$$

$$Variance = \sum_{i=1}^{N} \frac{(X_i - \bar{X})^2}{N} = \frac{(Mo100 - Mo100)^2}{1} = \frac{M_o^2(100-100)^2}{1} = 0 \quad (9)$$

The standard deviation, $s = \sqrt{Variance} = 0$ (10)

Here, we have one polymer chain and the average of one chain will be the same as that of the chain itself. This also explains why the standard deviation is identically zero. M_o represents the molecular weight of one building block (i.e., C_3H_6=42 g/mole).

$$PDI = \left(\frac{s}{\mu}\right)^2 + 1 = \frac{Variance}{\mu^2} + 1 = \left(\frac{0}{100Mo}\right)^2 + 1 = 1 \quad (11)$$

Eq. (11) simply says that if there is no deviation from the mean value, then all sampled polymer chains will lie on their mean value (i.e., a mono-disperse solution with $PDI = 1$).

It is worth mentioning here that Meira and Oliva [6] used such an equation in demonstrating the concept of poly dispersity index, where they exploited (PDI - 1) as a measure of the ratio between the absolute breadth of a number molar mass distribution (NMMD) and its arithmetic mean. PDI between 1.004 and 1.2 are typical of the narrow MMDs produced by living anionic polymerization; PDI between 1.5 and 3.0 are typical of conventional free-radical polymerizations; and PDI of 20 or higher are typical of polyolefins obtained via Ziegler-Natta catalysts [6].

Thus, $MWW = PDI \times MWN = 1 \times 100M_o = 100\, M_o$ (12)

The Second Case:

$$MWN = \frac{1\times50\times M_o + 1\times50\times M_o}{2} = 50M_o \quad (13)$$

$$\bar{X} = 50M_o \quad (14)$$

$$Variance = \sum_{i=1}^{2} \frac{(X_i - \bar{X})^2}{N} = \frac{M_o^2(50-50)^2 + M_o^2(50-50)^2}{2} = 0 \quad (15)$$

$$s = \sqrt{Variance} = 0 \quad (16)$$

$$PDI = \left(\frac{s}{\mu}\right)^2 + 1 = \frac{Variance}{\mu^2} + 1 = \frac{0}{\bar{X}^2} + 1 = 1 \quad (17)$$

Thus, $MWW = PDI \times MWN = 1 \times 50M_o = 50M_o$ (18)

Here, we have two polymer chains with identical number of blocks. Hence, the average will be equal to *50M*$_o$, which is the same as that of each chain.

<u>The Mono-Disperse Polymer</u>: In general, if we have one single chain with 100 blocks, two chains each with 50 blocks, four chains each with 25 blocks, and so on, then PDI will be one and MWN=MWW. Any of those separate cases, having equal chain length is called a mono-disperse polymeric system.

<u>The Third Case:</u>

$$MWN = \frac{1\times 60\times M_o + 1\times 40\times M_o}{2} = 50M_o \quad (19)$$

$$\bar{X} = 50M_o \quad (20)$$

$$Variance = \sum_{i=1}^{2} \frac{(X_i - \bar{X})^2}{N} = \frac{M_o^2(60-50)^2 + M_o^2(40-50)^2}{2} = 100M_o^2 \quad (21)$$

$$s = \sqrt{Variance} = 10M_o \quad (22)$$

$$PDI = \left(\frac{s}{\mu}\right)^2 + 1 = \left(\frac{10M_o}{50M_o}\right)^2 + 1 = 1.04 \quad (23)$$

Thus:

$$MWW = PDI \times MWN = 1.04 \times 50M_o = 52M_o \quad (24)$$

Here, we have two polymer chains with different number of blocks. Hence, the average will be equal to *50M*$_o$, which lies between *40Mo* and *60Mo*. Since we have a mixture containing two polymer chains but with different chain lengths, then PDI will be greater than one, reflecting the degree of scatter around the mean value (i.e., = *MWN*=$50M_o$). Notice that for such a case, if we apply Eq. (1) trice, we get:

$$\lambda_0 = \sum_{n=1}^{2} n^0 Q_n = 60^0 \times 1 + 40^0 \times 1 = 2 \quad (25)$$

$$\lambda_1 = \sum_{n=1}^{2} n^1 Q_n = 60^1 \times 1 + 40^1 \times 1 = 100 \quad (26)$$

$$\lambda_2 = \sum_{n=1}^{2} n^2 Q_n = 60^2 \times 1 + 40^2 \times 1 = 5{,}200 \quad (27)$$

Moreover, if we apply equations (2) through (6), we get:

DPN = λ_1/λ_0=100/2=50 (28)

DPW = λ_2/λ_1=5,200/100 = 52.0 (29)

$$PDI = DPW/DPN = (\lambda_2 \times \lambda_0)/(\lambda_1)^2 = (5{,}200 \times 2)/(100)^2 = 104/100 = 1.04 \quad (30)$$

$$MWN = DPN \times \bar{\mathrm{M}}_{\mathrm{segment}} = 50 \times M_o = \bar{X} \quad (31)$$

$$MWW = DPW \times \bar{\mathrm{M}}_{\mathrm{segment}} = 52 \times M_o \quad (32)$$

Notice that we have the same answer for PDI as given by equations (23) and (30); MWN is exactly $\bar{X}$; and MWW is the same as given by equations (24) and (32). We do not have to carry out the comparison between the methods anymore; this serves as an evidence that both methods quantitatively yield the same answer.

<u>The Fourth Case:</u>

$$MWN = \frac{(1\times 10\times M_o)+(1\times 20\times M_o)+(1\times 30\times M_o)+(1\times 40\times M_o)}{4} = 25M_o \quad (33)$$

$$\bar{X} = 25M_o \quad (34)$$

$$Variance = \sum_{i=1}^{2} \frac{(X_i-\bar{X})^2}{N} = \frac{M_o^2(40-25)^2+M_o^2(30-25)^2+M_o^2(20-25)^2+M_o^2(10-25)^2}{4} = 125M_o^2 \quad (35)$$

$$s = \sqrt{Variance} = 11.18M_o \quad (36)$$

$$PDI = \frac{Variance}{\mu^2} + 1 = \frac{125\,M_o^2}{(25M_o)^2} + 1 = 1.2 \quad (37)$$

Thus:

$$MWW = PDI \times MWN = 1.2 \times 25M_o = 30\,M_o \quad (38)$$

Here, we have four polymer chains with different number of blocks. Hence, the average will be equal to *$25M_o$*. Since we have a mixture containing four polymer chains but with different chain lengths, then PDI here will be greater than that of the third case, reflecting more degree of scatter around the mean value (i.e., $= MWN=25M_o$).

At the end, I hope that I managed to simplify for the reader the notion behind MWN, MWW, and PDI. Moreover, the “Madonna” portray is obviously more attractive than “Moment” portray in explaining the homo-polymer distribution properties.

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