An Extended Study on the Average Molecular Weights of Nonlinear Polymers

Lie-Ding Shiau

Department of Chemical Engineering, Chang Gung College of Medicine and Technology, Kweishan, Taoyuan, Taiwan, ROC

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ABSTRACT: A method is presented, based on the probability model proposed by Macosko and Miller, to calculate all the average molecular weights of nonlinear polymers. $\bar{M}_w$, $\bar{M}_z$, $\bar{M}_{z+1}$, and higher average molecular weights can be determined as a function of reaction extent directly without the calculation of the whole distribution. The results indicate that this approach can be easily formulated and applied for many nonlinear polymerization reactions.

1. Introduction

A quantitative description of the size distribution and the average size of any polymer is essential in the characterization of its physical properties. A number of theoretical models have already been developed to describe the resulting size distribution of polymers.[1-5] In these models, the formation of an infinite network was calculated statistically by considering the probability of continuation of the structure along any arbitrary chain. Thus, the whole distribution of the formed polymers can be described as a function of the reaction extent.

However, experimentally, rapid and frequently used techniques can only measure average molecular weights. Therefore, instead of the whole distribution, the average molecular weights appear to be sufficient for the recovery of experimental parameters describing the polymer system under investigation.

Gordon,[6] based on an adaptation of Good's stochastic theory of cascade processes,[7] employed the probability generating functions and derived the average properties directly for the polymer system, bypassing the calculation of the whole distribution. However, as indicated later by Macosko and Miller,[8] Gordon's method involves abstract mathematics and is rather difficult for formulating specific equations for the molecular weight averages.

To avoid use of abstract probability generating functions, Macosko and Miller[8-10] proposed a method for calculating the average properties of polymers directly. Starting with elementary probability and utilizing the recursive nature of the network polymers, $\bar{M}_w$ and $\bar{M}_z$ can be derived explicitly for a variety of polyfunctional polymerizations. However, $\bar{M}_{z+1}$ and higher average molecular weights were not determined in their work.

The aim of this paper is to derive a systematic method, based on the model presented by Macosko and Miller,[8] to calculate all the average molecular weights of nonlinear polymers. $\bar{M}_w$, $\bar{M}_z$, $\bar{M}_{z+1}$, and higher average molecular weights can be determined directly without the calculation of the whole distribution. In the derivation, we will retain Flory's simplifying assumptions:[1] (1) all functional groups of the same type are chemically equivalent and hence equally reactive; (2) the reactivity of a given group is independent of the size or structure of the molecule to which it is attached; (3) intramolecular reactions are forbidden.

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2. Theory

The following derivation basically follows the probability model presented by Macosko and Miller.[8] The major difference is that the concept of random variables will be applied here throughout the whole derivation instead of the expected values used in their paper. In Macosko and Miller's work,[8] only $\bar{M}_w$ and $\bar{M}_z$ can be calculated; $\bar{M}_{z+1}$ and higher averages cannot be computed. In the following, we will propose a new approach to derive $\bar{M}_w$, $\bar{M}_z$, $\bar{M}_{z+1}$, and higher average molecular weights.

Consider a copolymerization system consisting of C_a^0 moles of f functional A-type monomer (denoted as A_f) reacting with C_b^0 moles of g functional B-type monomer (denoted as B_g), as sketched in Figure 1. Let α represent the fraction of A groups which have reacted and β the fraction of B groups which have reacted. Then

$$f\alpha C_a^0 = g\beta C_b^0 \tag{1}$$

or

$$\beta = (fC_a^0/gC_b^0)\alpha = r\alpha \tag{2}$$

where $r = fC_a^0/(gC_b^0)$.

2.1. Macosko and Miller's Model and Weight-Average Molecular Weight ($\bar{M}_w$). In the analysis of the statistical properties of such a system, Macosko and Miller,[8] on the basis of elementary probability and the recursive nature of the network polymers, derived a method to calculate $\bar{M}_w$ and $\bar{M}_z$ as follows (eqs 3–10): Pick an A at random (in Figure 1). The random variable, W_A^{out}, is the weight attached to A looking out from its parent molecule in the direction $\xrightarrow{1}$. Then,

$$W_A^{out} = \begin{cases} 0 & \text{if A does not react} \\ W_B^{in} & \text{if A reacts (with B)} \end{cases}$$

where W_B^{in} is the weight attached to B looking along $\xrightarrow{2}$ into B's parent molecule. By the law of total probability for expectation, it can be written

$$\begin{aligned} E(W_A^{out}) &= E(W_A^{out}|\text{A reacts})P(\text{A reacts}) \\ &\quad + E(W_A^{out}|\text{A does not react}) \\ &\quad P(\text{A does not react}) \\ &= E(W_B^{in})\alpha + 0(1-\alpha) \\ &= \alpha E(W_B^{in}) \end{aligned} \tag{3}$$

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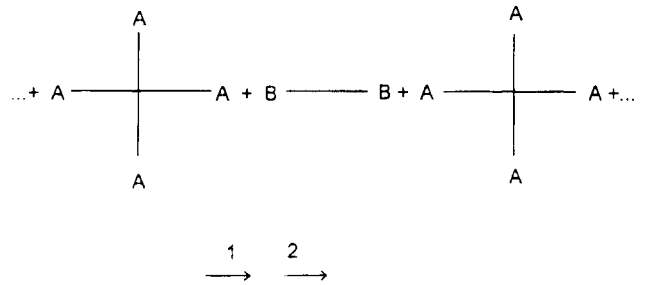

Figure 1. Polymerization between A_f and B_g (here, $f = 4, g = 2$).

A similar argument can be applied for W_B^{out}. Therefore,

$$E(W_B^{out}) = r\alpha E(W_A^{in}) \tag{4}$$

Considering the polymerization between A and B (see Figure 1), they derive

$$W_A^{in} = M_a + \sum_{i=1}^{f-1} W_{A,i}^{out} \tag{5}$$

where M_a is the molecular weight of A_f and $W_{A,i}^{out}$ is the weight attached to the ith branch of a randomly chosen A_f.

$$W_B^{in} = M_b + \sum_{i=1}^{g-1} W_{B,i}^{out} \tag{6}$$

where M_b is the molecular weight of B_g and $W_{B,i}^{out}$ is the weight attached to the ith branch of a randomly chosen B_g. This set of two equations (eqs 5 and 6) will recycle due to the recursive nature of the structure. Taking the expectation of eqs 5 and 6 leads to (see Appendix A)

$$E(W_A^{in}) = M_a + (f-1)E(W_A^{out}) \tag{7}$$

$$E(W_B^{in}) = M_b + (g-1)E(W_B^{out}) \tag{8}$$

By substitution of eqs 3 and 4 into eqs 7 and 8, $E(W_A^{out})$, $E(W_B^{out})$, $E(W_A^{in})$, and $E(W_B^{in})$ can be solved.

The molecular weight, W_A, of the entire molecule to which a randomly chosen A belongs, will just be the molecular weight of A_f plus the weights attached to f functional groups looking out from each functional group. Therefore,

$$W_A = M_a + \sum_{i=1}^{f} W_{A,i}^{out} \tag{9}$$

Taking the expectation of this equation leads to (see Appendix A)

$$E(W_A) = M_a + fE(W_A^{out}) \tag{10}$$

A similar argument can be applied for W_B. Therefore,

$$W_B = M_b + \sum_{i=1}^{g} W_{B,i}^{out} \tag{11}$$

Taking the expectation of this equation leads to

$$E(W_B) = M_b + gE(W_B^{out}) \tag{12}$$

$\bar{M}_w$, by definition, is the first moment, $E(W)$.

$$\bar{M}_w = E(W) = q_a E(W_A) + q_b E(W_B) \tag{13}$$

where

$$q_a = C_a^0 M_a/(C_a^0 M_a + C_b^0 M_b) \tag{14}$$

$$q_b = C_b^0 M_b/(C_a^0 M_a + C_b^0 M_b) \tag{15}$$

Note that C_a^0 and C_b^0 are the initial concentrations of A_f and B_g respectively. M_a and M_b are the molecular weights of A_f and B_g, respectively. Therefore, q_a and q_b represent the initial weight fractions of A_f and B_g in the system, respectively. Substituting and rearranging give

$$\bar{M}_w = q_a\,(M_a + f\alpha\,(r\alpha(g-1)\,M_a + M_b))/(1 - r\alpha^2\,(f-1)(g-1)) + q_b(M_b + gr\alpha(M_a + \alpha\,(f-1)M_b))/(1 - r\alpha^2\,(f-1)(g-1)) \tag{16}$$

The value of α at which $\bar{M}_w$ diverges is called the gel point (α_{gel}). As shown in eq 16, $\bar{M}_w$ becomes infinite when

$$\alpha_{gel}^2 = 1/(r(f-1)(g-1)) \tag{17}$$

2.2. Z-Average Molecular Weight ($\bar{M}_z$). $\bar{M}_z$, by definition, is the ratio of the second moment of the weight distribution, $E(W^2)$, to the first moment, $E(W)$. Note that $\bar{M}_w$ represents $E(W)$. Thus,

$$\bar{M}_z = E(W^2)/E(W) \tag{18}$$

Macosko and Miller[8] proposed a method to calculate $E(W^2)$ from the variance of W. In this paper, we will use a different approach. The advantage of our approach is that it can be extended to calculate $\bar{M}_{z+1}$ and higher averages. We will derive $E(W^2)$ as follows. Taking the square on both sides of eqs 5 and 6 yields

$$(W_A^{in})^2 = M_a^2 + 2M_a\,(\sum_{i=1}^{f-1} W_{A,i}^{out}) + (\sum_{i=1}^{f-1} W_{A,i}^{out})^2 \tag{19}$$

$$(W_B^{in})^2 = M_b^2 + 2M_b\,(\sum_{i=1}^{g-1} W_{B,i}^{out}) + (\sum_{i=1}^{g-1} W_{B,i}^{out})^2 \tag{20}$$

Taking the expectation of the above equations gives (see Appendix A)

$$E((W_A^{in})^2) = M_a^2 + 2\,(f-1)M_a E(W_A^{out}) + (f-1)E((W_A^{out})^2) + (f-1)(f-2)(E(W_A^{out}))^2 \tag{21}$$

$$E((W_B^{in})^2) = M_b^2 + 2(g-1)M_b E(W_B^{out}) + (g-1)E((W_B^{out})^2) + (g-1)(g-2)(E(W_B^{out}))^2 \tag{22}$$

Similar to the development of eqs 3 and 4, if the random

variables $(W_A^{out})^2$ and $(W_B^{out})^2$ are used instead of W_A^{out} and W_B^{out}, respectively, we have

$$E((W_A^{out})^2) = \alpha E((W_B^{in})^2) \quad (23)$$

$$E((W_B^{out})^2) = r\alpha E((W_A^{in})^2) \quad (24)$$

Thus, eqs 21–24 can be solved simultaneously for $E((W_A^{in})^2)$, $E((W_B^{in})^2)$, $E((W_A^{out})^2)$, and $E((W_B^{out})^2)$.

Taking the square on both sides of eqs 9 and 11 yields

$$W_A^2 = M_a^2 + 2M_a(\sum_{i=1}^{f} W_{A,i}^{out}) + (\sum_{i=1}^{f} W_{A,i}^{out})^2 \quad (25)$$

$$W_B^2 = M_b^2 + 2M_b(\sum_{i=1}^{g} W_{B,i}^{out}) + (\sum_{i=1}^{g} W_{B,i}^{out})^2 \quad (26)$$

Taking the expectation of the above equations gives (see Appendix A)

$$E(W_A^2) = M_a^2 + 2fM_aE(W_A^{out}) + fE((W_A^{out})^2) + f(f-1)(E(W_A^{out}))^2 \quad (27)$$

$$E(W_B^2) = M_b^2 + 2gM_bE(W_B^{out}) + gE((W_B^{out})^2) + g(g-1)(E(W_B^{out}))^2 \quad (28)$$

Then, $E(W^2)$ can be expressed as

$$E(W^2) = q_aE(W_A^2) + q_bE(W_B^2) \quad (29)$$

where q_a and q_b are defined in eqs 14 and 15. Substituting eqs 27 and 28 into eq 29, we can obtain a complete formula for $E(W^2)$. Thus, M_z can be calculated by eq 18. Note that M_z derived in this paper agrees with the result obtained by Macosko and Miller from the variance of W.[8]

2.3. $Z+1$-Average Molecular Weight (M_{z+1}) and Higher Average Molecular Weights. M_{z+1}, by definition, is the ratio of the third moment of the weight distribution, $E(W^3)$, to the second moment, $E(W^2)$. Thus,

$$M_{z+1} = E(W^3)/E(W^2) \quad (30)$$

The expression for $E(W^3)$ will be derived in the following. Taking the third power on both sides of eqs 5 and 6 yields

$$(W_A^{in})^3 = M_a^3 + 3M_a^2(\sum_{i=1}^{f-1} W_{A,i}^{out}) + 3M_a(\sum_{i=1}^{f-1} W_{A,i}^{out})^2 + (\sum_{i=1}^{f-1} W_{A,i}^{out})^3 \quad (31)$$

$$(W_B^{in})^3 = M_b^3 + 3M_b^2(\sum_{i=1}^{g-1} W_{B,i}^{out}) + 3M_b(\sum_{i=1}^{g-1} W_{B,i}^{out})^2 + (\sum_{i=1}^{g-1} W_{B,i}^{out})^3 \quad (32)$$

Taking the expectation of the above equations gives (see Appendix A)

$$E((W_A^{in})^3) = M_a^3 + 3(f-1)M_a^2E(W_A^{out}) + 3(f-1)M_aE((W_A^{out})^2) + 3(f-1)(f-2)M_a(E(W_A^{out}))^2 + (f-1)E((W_A^{out})^3) + 3(f-1)(f-2)E((W_A^{out})^2)E(W_A^{out}) + (f-1)(f-2)(f-3)(E(W_A^{out}))^3 \quad (33)$$

$$E((W_B^{in})^3) = M_b^3 + 3(g-1)M_b^2E(W_B^{out}) + 3(g-1)M_bE((W_B^{out})^2) + 3(g-1)(g-2)M_b(E(W_B^{out}))^2 + (g-1)E((W_B^{out})^3) + 3(g-1)(g-2)E((W_B^{out})^2)E(W_B^{out}) + (g-1)(g-2)(g-3)(E(W_B^{out}))^3 \quad (34)$$

Similar to the development of eqs 3 and 4, if the random variables $(W_A^{out})^3$ and $(W_B^{out})^3$ are used instead of W_A^{out} and W_B^{out}, respectively, we have

$$E((W_A^{out})^3) = \alpha E((W_B^{in})^3) \quad (35)$$

$$E((W_B^{out})^3) = r\alpha E((W_A^{in})^3) \quad (36)$$

Thus, eqs 33–36 can be solved simultaneously for $E((W_A^{in})^3)$, $E((W_B^{in})^3)$, $E((W_A^{out})^3)$, and $E((W_B^{out})^3)$.

Taking the third power on both sides of eqs 9 and 11 yields

$$W_A^3 = M_a^3 + 3M_a^2(\sum_{i=1}^{f} W_{A,i}^{out}) + 3M_a(\sum_{i=1}^{f} W_{A,i}^{out})^2 + (\sum_{i=1}^{f} W_{A,i}^{out})^3 \quad (37)$$

$$W_B^3 = M_b^3 + 3M_b^2(\sum_{i=1}^{g} W_{B,i}^{out}) + 3M_b(\sum_{i=1}^{g} W_{B,i}^{out})^2 + (\sum_{i=1}^{g} W_{B,i}^{out})^3 \quad (38)$$

Taking the expectation of the above equations gives (see Appendix A)

$$E(W_A^3) = M_a^3 + 3fM_a^2E(W_A^{out}) + 3fM_aE((W_A^{out})^2) + 3f(f-1)M_a(E(W_A^{out}))^2 + fE((W_A^{out})^3) + 3f(f-1)E((W_A^{out})^2)E(W_A^{out}) + f(f-1)(f-2)(E(W_A^{out}))^3 \quad (39)$$

$$E(W_B^3) = M_b^3 + 3gM_b^2E(W_B^{out}) + 3gM_bE((W_B^{out})^2) + 3g(g-1)M_b(E(W_B^{out}))^2 + gE((W_B^{out})^3) + 3g(g-1)E((W_B^{out})^2)E(W_B^{out}) + g(g-1)(g-2)(E(W_B^{out}))^3 \quad (40)$$

Then, $E(W^3)$ can be expressed as

$$E(W^3) = q_a E(W_A{}^3) + q_b E(W_B{}^3) \quad (41)$$

Substituting eqs 39 and 40 into eq 41, we can obtain a complete formula for $E(W^3)$. Thus, $\bar{M}_{z+1}$ can be calculated by eq 30.

Higher moments of the molecular weight distribution can be derived in the similar approach. In general, $E(W^n)$ can be developed by taking the nth power on both sides of eqs 5 and 6 and repeating the calculations as described above. Thus,

$$(W_A{}^{in})^n = M_a{}^n + nM_a{}^{n-1}(\sum_{i=1}^{f-1} W_{A,i}{}^{out}) + \frac{n(n-1)}{2!}M_a{}^{n-2}(\sum_{i=1}^{f-1} W_{A,i}{}^{out})^2 + \frac{n(n-1)(n-2)}{3!}M_a{}^{n-3}(\sum_{i=1}^{f-1} W_{A,i}{}^{out})^3 + \ldots + (\sum_{i=1}^{f-1} W_{A,i}{}^{out})^n \quad (42)$$

$$(W_B{}^{in})^n = M_b{}^n + nM_b{}^{n-1}(\sum_{i=1}^{g-1} W_{B,i}{}^{out}) + \frac{n(n-1)}{2!}M_b{}^{n-2}(\sum_{i=1}^{g-1} W_{B,i}{}^{out})^2 + \frac{n(n-1)(n-2)}{3!}M_b{}^{n-3}(\sum_{i=1}^{g-1} W_{B,i}{}^{out})^3 + \ldots + (\sum_{i=1}^{g-1} W_{B,i}{}^{out})^n \quad (43)$$

As described before, $E((W_A{}^{in})^n)$ and $E((W_B{}^{in})^n)$ can be obtained by taking the expectation of the above equations (see Appendix A). Similar to the development of eqs 3 and 4, the random variable $(W_A{}^{out})^n$ and $(W_B{}^{out})^n$ is used instead of $W_A{}^{out}$ and $W_B{}^{out}$, respectively, we have

$$E((W_A{}^{out})^n) = \alpha E((W_B{}^{in})^n) \quad (44)$$

$$E((W_B{}^{out})^n) = r\alpha E((W_A{}^{in})^n) \quad (45)$$

Thus, $E((W_A{}^{in})^n)$, $E((W_B{}^{in})^n)$, $E((W_A{}^{out})^n)$, and $E((W_B{}^{out})^n)$ can be solved simultaneously.

Taking the $n$the power on both sides of eqs 9 and 11 yields

$$(W_A)^n = M_a{}^n + nM_a{}^{n-1}(\sum_{i=1}^{f} W_{A,i}{}^{out}) + \frac{n(n-1)}{2!}M_a{}^{n-2}(\sum_{i=1}^{f} W_{A,i}{}^{out})^2 + \frac{n(n-1)(n-2)}{3!}M_a{}^{n-3}(\sum_{i=1}^{f} W_{A,i}{}^{out})^3 + \ldots + (\sum_{i=1}^{f} W_{A,i}{}^{out})^n \quad (46)$$

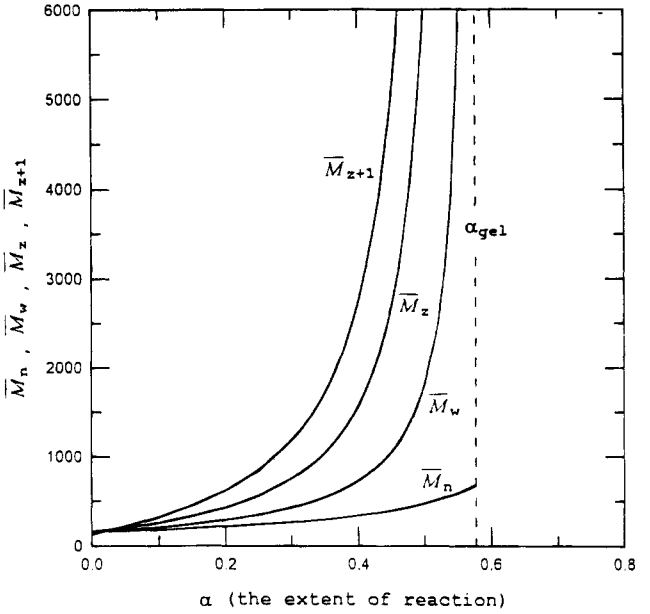

Figure 2. $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, and $\bar{M}_{z+1}$ versus extent of reaction (in this example, $M_a = 136$, $M_b = 168$, $f = 4$, $g = 2$, $C_a{}^0 = 1$, and $C_b{}^0 = 2$).

$$(W_B)^n = M_b{}^n + nM_b{}^{n-1}(\sum_{i=1}^{g} W_{B,i}{}^{out}) + \frac{n(n-1)}{2!}M_b{}^{n-2}(\sum_{i=1}^{g} W_{B,i}{}^{out})^2 + \frac{n(n-1)(n-2)}{3!}M_b{}^{n-3}(\sum_{i=1}^{g} W_{B,i}{}^{out})^3 + \ldots + (\sum_{i=1}^{g} W_{B,i}{}^{out})^n \quad (47)$$

In a similar way as before, $E(W_A{}^n)$ and $E(W_B{}^n)$ can be obtained by taking the expectation of the above equations (see Appendix A). Then, $E(W^n)$ can be expressed as

$$E(W^n) = q_a E(W_A{}^n) + q_b E(W_B{}^n) \quad (48)$$

Substituting $E(W_A{}^n)$ and $E(W_B{}^n)$ into eq 48, we can obtain a complete formula for $E(W^n)$.

2.4. Number-Average Molecular Weight ($\bar{M}_n$). Calculated from stoichiometry, $\bar{M}_n$ is just the total mass, m_{total}, divided by the number of molecules present, n. Then,

$$\bar{M}_n = m_{total}/n \quad (49)$$

where

$$m_{total} = C_a{}^0 M_a + C_b{}^0 M_b \quad (50)$$

$$n = C_a{}^0 + C_b{}^0 - \alpha f C_a{}^0 \quad (51)$$

Thus,

$$\bar{M}_n = (C_a{}^0 M_a + C_b{}^0 M_b)/(C_a{}^0 + C_b{}^0 - \alpha f C_a{}^0) \quad (52)$$

3. Results and Discussion

A model is presented in this paper, without the calculation of whole distribution, to determine $\bar{M}_w$, $\bar{M}_z$, $\bar{M}_{z+1}$, and higher average molecular weights as a function of reaction extent for nonlinear polymers. Numerical results of the developed model are illustrated in Figure 2 for urethane formation from pentaerythritol and hexamethylene diisocyanate. It is obvious that $\bar{M}_n < \bar{M}_w < \bar{M}_z < \bar{M}_{z+1}$, which is in agreement with the definition of these average properties. Note that $\bar{M}_n$ is finite at the gel point.

$\bar{M}_w$ and $\bar{M}_z$ computed from this paper are identical with the results computed by Macosko and Miller.[8] However, our method also allows one to calculate $\bar{M}_{z+1}$ and higher average molecular weights. The results indicate that this approach can be easily formulated and applied for many nonlinear polymerization reactions.

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Appendix A

Based on probability theory in most texts,[11] if $X_1, X_2, \ldots, X_f$ are independent random variables with the same distribution, X, then

$$E(\sum_{i=1}^{f} X_i) = \sum_{i=1}^{f} E(X_i) = fE(X) \tag{A1}$$

$$\begin{aligned} E(\sum_{i=1}^{f} X_i)^2 &= E(\sum_{i=1}^{f} X_i^2 + \sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f} X_iX_j) \\ &= E(\sum_{i=1}^{f} X_i^2) + E(\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f} X_iX_j) \\ &= \sum_{i=1}^{f} E(X_i^2) + \sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f} E(X_i)E(X_j) \\ &= fE(X^2) + f(f-1)(E(X))^2 \end{aligned} \tag{A2}$$

$$\begin{aligned} E(\sum_{i=1}^{f} X_i)^3 &= E(\sum_{i=1}^{f} X_i^3 + 3\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f} X_i^2X_j + \sum_{i=1}^{f}\sum_{j=1,j\neq ik=1,k\neq i\neq j}^{f}\sum^{f} X_iX_jX_k) \\ &= E(\sum_{i=1}^{f} X_i^3) + 3E(\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f} X_i^2X_j) + E(\sum_{i=1}^{f}\sum_{j=1,j\neq ik=1,k\neq i\neq j}^{f}\sum^{f} X_iX_jX_k) \\ &= \sum_{i=1}^{f} E(X_i^3) + 3\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f} E(X_i^2)E(X_j) + \sum_{i=1}^{f}\sum_{j=1,j\neq ik=1,k\neq i\neq j}^{f}\sum^{f} E(X_i)E(X_j)E(X_k) \\ &= fE(X^3) + 3f(f-1)E(X^2)E(X) + f(f-1)(f-2)(E(X))^3 \end{aligned} \tag{A3}$$

$$\begin{aligned} E(\sum_{i=1}^{f} X_i)^n &= E\left(\sum_{\substack{n_1,n_2,\ldots,n_f\geq 0 \\ (n_1+n_2+\ldots+n_f=n)}}^{n} \frac{n!}{n_1!n_2!\ldots n_f!} X_1^{n_1}X_2^{n_2}\ldots X_f^{n_f}\right) \\ &= \sum_{\substack{n_1,n_2,\ldots,n_f\geq 0 \\ (n_1+n_2+\ldots+n_f=n)}}^{n} \frac{n!}{n_1!n_2!\ldots n_f!} E(X_1^{n_1}X_2^{n_2}\ldots X_f^{n_f}) \\ &= \sum_{\substack{n_1,n_2,\ldots,n_f\geq 0 \\ (n_1+n_2+\ldots+n_f=n)}}^{n} \frac{n!}{n_1!n_2!\ldots n_f!} E(X_1^{n_1})E(X_2^{n_2})\ldots E(X_f^{n_f}) \\ &= \sum_{\substack{n_1,n_2,\ldots,n_f\geq 0 \\ (n_1+n_2+\ldots+n_f=n)}}^{n} \frac{n!}{n_1!n_2!\ldots n_f!} E(X^{n_1})E(X^{n_2})\ldots E(X^{n_f}) \end{aligned} \tag{A4}$$

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