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NEW INTERPRETATIONS

Derivation of the Molecular Weight Distribution for Random Condensation Polymerization as a Special Case of the Binomial Distribution

INTRODUCTION

One of the simplest polymerization mechanisms arises during the course of forming linear condensation polymers by the intermolecular reaction of bifunctional compounds.

Flory [1]derived the molecular weight distribution during random condensation by assuming that all unreactive end groups have equal potential for reaction. He defined a parameter, p, the fraction of reacted end groups, as:

$$p = (n_O - N) / n_O \tag{1}$$

where N = number of unreacted end groups which remain after the reaction has proceeded for a time t, and $n_O - N$ = number of reacted end groups.

Flory obtained the distribution of molecules, P_X, in terms of p:

$$P_X = xp^{x-1} (1 - p)^2 \tag{2}$$

where P_X is the probability of forming a molecule containing x segments. A segment represents a monomer molecule (x = 1) or its radical.

Equation (2) looks suspiciously like that distribution obtained by considering a random walk in one dimension, the binomial distribution. It is shown in the following section that the molecular weight distribution for random condensation polymerization can be directly obtained as a special case of the binomial distribution.

RANDOM CONDENSATION DISTRIBUTION AS A SPECIAL CASE OF THE BINOMIAL DISTRIBUTION

Consider a particle initially located at some point in space, which will be labeled as the origin. The particle is constrained to move in discrete steps of equal length along a straight line either to the left or the right of the origin. Each new step of the particle is independent of the direction and position of the immediately previous step.

Let n_1 = number of steps taken to the right.

n_2 = number of steps taken to the left.

N = total number of steps = $n_1 + n_2$.

Because the steps are assumed to be statistically independent, a single probability unequivocally characterizes each step.

Let p = probability that any given step is taken to the right; then $(1 - p)$ = probability that any given step is taken to the left.

The probability $P(n_1)$ of taking n_1 steps to the right (and n_2 to the left) out of a total of N is given by [2]:

$$P(n_1) = \frac{N!}{n_1!\, n_2!}\, p^{n_1} (1 - p)^{n_2} \tag{3}$$

The distribution in Eq. (3) is called the binomial distribution because the expression for $P(n_1)$ represents a general term obtained in expanding $(p + q)^N$ by the binomial theorem. Recall that

$$(p + q)^N = \sum_{n=0}^{N} \frac{N}{n!\,(N - n)!}\, p^n\, q^{N-n} \tag{4}$$

It is easy to show that Eq. (3) is indeed a probability distribution by using Eq. (4). Let $q = 1 - p$ in Eq. (4). The left side is identically 1 and each term on the right side is $P(n_1)$, $n_1 = 0.\ 1,\ 2 \ldots N$. Thus, Eq. (3) is normalized and is indeed a probability distribution.

The probability distribution for random condensation polymerization, Eq. (1), is obtained as a special case of the binomial distribution, Eq. (3), as follows: Consider a random walk in one dimension in which a particle is allowed to take n_1 steps to the right and one step to the left out of a total of N ($=n_1 + 1$) steps. The n_1 steps to the right represent the n_1 linkages between the N segments of an N-mer. The one step to the left represents the unreacted site remaining on one end of the polymer chain.

Including the unreacted site at the other end of the chain will occur in a quite natural way at the end of the derivation.

The probability distribution arising from this special case can be extracted immediately from Eq. (3).

$$P_{(N-1)} \; (= P(n_1)) = \frac{N!}{(N-1)!\,1!} \; p^{N-1} (1-p)^1 \tag{5}$$

Writing the combinatorial term explicitly we obtain:

$$P_{(N-1)} = Np^{N-1} (1-p)^1 \tag{6}$$

The binomial distribution, Eq. (3), was shown to be normalized by summing over all values of n_1 up to and including $n_1 = N$, where N was arbitrary but fixed. In obtaining the result shown in Eq. (6) for the special case of $n_1 = N - 1$, we have fixed n_1 in terms of N. Therefore, to determine whether Eq. (6) is normalized, we must sum over all possible values of N. Such a sum will include chains of 1, 2, 3, . . . $^{\infty}$ segments in the polymerization vessel.

$$\sum_{N=1}^{\infty} P_{(N-1)} = \sum_{N=1}^{\infty} Np^{N-1} (1-p)^1 \tag{7}$$

The term $(1-p)^1$ does not enter into the summation and can be placed outside.

$$\sum_{N=1}^{\infty} P_{(N-1)} = (1-p)^1 \sum_{N=1}^{\infty} Np^{N-1} \tag{8}$$

(The series $\sum_{N=1}^{\infty} p^{N-1} = 1/(1-p)$. This well-known geometric series valid when $p < 1$ can be differentiated [3] to immediately obtain the required result for Eq. (8)).

$$\sum_{N=1}^{\infty} Np^{N-1} = \frac{1}{(1-p)^2} \tag{9}$$

Substituting the right-hand side of Eq. (9) into Eq. (8) we obtain:

$$\sum_{N=1}^{\infty} P_{(N-1)} = (1-p)^1 \times \frac{1}{(1-p)^2} = \frac{1}{(1-p)} \tag{10}$$

Rearranging Eq. (10),

$$(1-p) \sum_{N=1}^{\infty} P_{(N-1)} = 1 \tag{11}$$

Equation (7) is thus not normalized but possesses a normalizing factor of (1 - p). By the earlier definition, this factor is the probability that no linkage exists between two arbitrarily chosen segments. The normalizing factor (1 - p) obtained in Eq. (11) now accounts for the reactive end group at the other end of the chain.

The results are summarized as follows: Multiplying both sides of Eq. (6) by (1 - p) yields

$$(1-p) P_{(N-1)} = Np^{N-1}(1-p)^2 \tag{12}$$

Recall that the subscript N - 1 occurring on the left side of Eq. (12) represents the N - 1 linkages in a chain of N segments. The subscript x in the left side of Eq. (2) represented a chain of x segments. Rewriting Eq. (12) in the notation of Eq. (2) yields

$$(1-p) P_{(N-1)} = P_x = xp^{x-1}(1-p)^2 \tag{13}$$

The very general binomial distribution has thus yielded as a particular result the molecular weight distribution obtained in random condensation polymerization.

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