A New Derivation of Molecular Size Distribution in Nonlinear Polymers[1]

Johnson F. Yan

Weyerhaeuser Company, Research and Engineering, Seattle, Washington 98134.
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ABSTRACT: A generalized molecular size distribution for both linear and nonlinear polymers has the form of a power series distribution. From a well-known property of the power series distribution, the size distribution can be generated from the expressions of number and weight average sizes. These averages are readily obtainable from a stoichiometry consideration and a simple stochastic branching process. Examples are given for the Flory–Stockmayer distributions for nonlinear polymers obtained by condensation of RA_f and ARB_{f-1} types of monomers.

In 1943, Stockmayer derived a general expression for the molecular size distribution obtained by the self-condensation of a monomer RA_f.[2,3] When the number of functional groups, f, is three or more, the distribution becomes quite complicated. Nevertheless, since it is one of the most fundamental size distributions for nonlinear polymers, extensive discussion has been continued for more than three decades.[4] In the meantime, new derivations continue to appear in the literature.[5,6]

Both Stockmayer[2] and Flory[3] used conventional combinatory arguments in their derivations; Stockmayer also provided a kinetic scheme associated with this distribution.[2] More recent derivations are those using generating functions in the cascade theory developed by Good,[5] Whittle,[6] and Gordon and co-workers.[7] Their results essentially confirmed the validity of the Flory–Stockmayer distribution.

We outline below still another method of arriving at this distribution by using a well-known property of the power series distributions.

Basic Assumptions and Formulation

We retain the following simple assumptions made by other workers[2-8] for the condensation of RA_f type monomers at any stage of reaction: (a) all functional groups A's are equally reactive; (b) no intramolecular reactions occur; (c) the weight of material lost during condensation is negligible.

The first two assumptions are usually made, and their constraints have been extensively discussed by other workers.[2-8] The last assumption is equally important for our dealing with number and weight average sizes. Before gelation occurs, we can assume the existence of a number distribution and its first two moments. This distribution is denoted by $p(n)$ and identified as the number fraction of an n-mer.

Denoting the number average size by $\bar{n}$ and the weight average by $\bar{n}_w$, these averages are related to the second cumulant κ_2 or the variance σ^2 of the distribution by

$$\kappa_2 = \sigma^2 = \bar{n}\bar{n}_w - \bar{n}^2 \tag{1}$$

The number average is also the first cumulant κ_1.

The most important feature in this derivation is that we recognize a size distribution has the form of a generalized power series distribution.[9,10] This form of discrete distribution is valid for all polymers, linear and nonlinear (see eq 5 in Stockmayer's first paper[2]). The power series distribution $p(n)$ is defined for polymers by

$$p(n) = a_n\theta^n/F(\theta)$$

$$n = 1, 2, \ldots; a_n \geq 0, \theta > 0 \tag{2}$$

where

$$F(\theta) = \sum_{n=1}^{\infty} a_n\theta^n \tag{3}$$

is called the series function. The distribution is normalized.

An important property of the power series distributions is that the first two cumulants, and hence the first two moments, are sufficient to determine the entire distribution, provided that these cumulants are functions of another parameter α. This result is expressed by Khatri in the following form:[9,10]

$$\frac{\mathrm{d}\ln\theta}{\mathrm{d}\alpha} = \frac{\mathrm{d}\kappa_1(\alpha)}{\mathrm{d}\alpha}\Big/\kappa_2(\alpha) \tag{4}$$

$$\frac{\mathrm{d}\ln F(\theta)}{\mathrm{d}\alpha} = \frac{\mathrm{d}\kappa_1(\alpha)}{\mathrm{d}\alpha}\cdot\frac{\kappa_1(\alpha)}{\kappa_2(\alpha)} \tag{5}$$

These two equations determine the distribution parameter θ and the series function F.

Alternately, the last two equations may be combined to

$$\frac{\mathrm{d}\ln F(\theta)}{\mathrm{d}\ln\theta} = \kappa_1(\alpha) \tag{6}$$

Therefore the distribution is determined by the expressions of κ_1 and θ, if the form of $\theta(\alpha)$ is readily obtainable.

We will identify the parameter α as the branching probability, or the reacted fraction of the functional groups A.[2,3] The series function $F(\theta)$ thus determined may be a function of α, namely $F(\theta(\alpha))$; in this case it will also be denoted by $\phi(\alpha)$.

Condensation of a RA_f Monomer

An example of this condensation is the etherification of pentaerythritol ($f = 4$). The number average is obtained by a simple stoichiometry calculation:[2,8]

$$\bar{n} = (1 - \alpha f/2)^{-1} \tag{7}$$

The weight average is obtained by a more elaborate scheme, but it still can be calculated directly without a priori knowledge of the distribution.

A simple stochastic derivation has been given by Macosko and Miller.[8] Their result is in agreement with Flory[3] and Stockmayer:[2]

$$\bar{n}_w = (1 + \alpha)/[1 - (f - 1)\alpha] \tag{8}$$

From the last two equations and eq 1 we obtain

$$\kappa_2 = (f\alpha/2)(1 - \alpha)/[1 - (f - 1)\alpha](1 - \alpha f/2)^2 \tag{9}$$

$$\mathrm{d}\kappa_1/\mathrm{d}\alpha = (f/2)(1 - \alpha f/2)^{-2}$$

Simple manipulation yields

$$\frac{\mathrm{d}\ln\theta}{\mathrm{d}\alpha} = \frac{1}{\alpha} + \frac{2 - f}{1 - \alpha}$$

$$\frac{\mathrm{d}\ln F}{\mathrm{d}\alpha} = \frac{1}{\alpha} + \frac{2}{1 - \alpha} - \frac{(f/2)}{1 - f\alpha/2}$$

Therefore

$$\theta(\alpha) = \alpha(1 - \alpha)^{f-2} \tag{10}$$

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$$\phi(\alpha) = F(\theta(\alpha)) = \alpha(1 - f\alpha/2)(1 - \alpha)^{-2} \tag{11}$$

Since a_n is the coefficient of θ^n in the expansion of $F(\theta)$, the conversion between parameters α and θ is provided by Good's theorem of Langrange's expansion.[5,6] Using our notation in this theorem, let

$$g(\alpha) = (1 - \alpha)^{-(f-2)}; \quad \theta = \alpha/g(\alpha)$$

we have

$$\begin{aligned} a_n &= \text{coeff. of } \theta^n \text{ in } F(\theta) \\ &= (1/n) \text{ coeff. of } \alpha^{n-1} \text{ in } \phi'(\alpha)[g(\alpha)]^n \end{aligned} \tag{12}$$

Since

$$\phi'(\alpha) = [1 - (f - 1)\alpha](1 - \alpha)^{-3}$$

we have

$$na_n = \binom{fn - n + 1}{n - 1} - (f - 1)\binom{fn - n}{n - 2}$$

or

$$a_n = \frac{f}{n(n - 1)}\binom{fn - n}{n - 2} \tag{13}$$

In terms of α, the power series distribution emerges as

$$\begin{aligned} p(n) &= a_n\theta^n/\phi(\alpha) \\ &= \frac{f(fn - n)!}{(1 - f\alpha/2)n!(fn - 2n + 2)!}\alpha^{n-1}(1 - \alpha)^{fn-2n+2} \end{aligned} \tag{14}$$

in agreement with that derived by other methods.[2,3,5,7]

Condensation of ARB_{f-1} Monomers

This reaction has been treated by Flory.[3] In this condensation, A may react with B, but reactions between like functional groups are forbidden. In terms of the branching probability α (which in this case is the reacted fraction of B groups), the averages are given by[3]

$$\bar{n} = [1 - \alpha(f - 1)]^{-1} \tag{15}$$

$$\bar{n}_w = [1 - \alpha^2(f - 1)][1 - \alpha(f - 1)]^{-2} \tag{16}$$

Proceeding with the same technique as used in the last section, we have the same expression for θ, but the series function takes a simpler form

$$\phi(\alpha) = \alpha(1 - \alpha)^{-1}$$

Use of Good's theorem gives

$$na_n = \binom{fn - n}{n - 1}.$$

Finally we have

$$p(n) = \frac{1 - \alpha}{\alpha n}\binom{fn - n}{n - 1}\alpha^n(1 - \alpha)^{fn-2n} \tag{17}$$

which is again in agreement with Flory.[3]

In the condensation of both types (RA_f and ARB_{f-1}) of monomers, the assumption of equal reactivity allows the immediate evaluation of the distribution parameter $\theta(\alpha)$. Since an n-mer contains $n - 1$ linkages and $fn - 2n + 2$ unreacted groups, the probability of forming any n-meric configuration is[2,3]

$$\alpha^{n-1}(1 - \alpha)^{fn-2n+2}$$

With comparison of this probability with the factor θ^n in eq 2, we obtain directly the form of θ as given in eq 10. In this way, the distributions in eq 14 and 17 can be derived without the knowledge of the weight average size.

Discussion

For years we have been working toward a simplified and unified treatment of the molecular size distributions;[11] the identification of the size distribution as a power series distribution has partially achieved this goal. As a consequence of this identification, we conclude that a size distribution, a probability generating function, and a knowledge of number and weight averages yield the same degree of information on the distribution itself, provided that the averages can be expressed in terms of a single parameter.

So far, we have only discussed the number distribution but not the weight distribution (weight fraction of an n-mer). The latter is given by

$$p_1(n) = \frac{n}{\bar{n}}p(n)$$

In the nonlinear polymer case, the normalization of $p_1(n)$ is associated with gelation. In essence, $p_1(n)$ is normalized to unity in the pregelation stage; after the gel point the sum $\sum p_1(n)$ over all finite species is the weight fraction of the sol.[2,3,5]

It is interesting to note that the weight distribution associated with eq 14 is a special case of the generalized negative binominal distribution, which in turn is one of the Lagrange distributions.[12] The generation of a series of Lagrange distributions, like the generating function[5] and the power series methods, also involves the use of the Lagrange expansion. Similarly, the distribution in eq 17 is a special case of Consul distribution, which is also one of the Lagrange distributions.[12] Therefore, there may be other applications of Lagrange distributions in nonlinear polymers.

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References and Notes

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