increases, the downfield peak increases in intensity and the upfield peak decreases in relative intensity. This fact suggested to us that the effect might reflect differential solvation of the chain ends and the chain interior by the aromatic solvent. Toward that end it was particularly interesting to consider the ^{1}H NMR spectrum of linear polyethylene, reported in Liu's first paper. In that spectrum only a single broad line is observed. Chain folding implies for a long polymer many loops and many tails. For polyethylene the doublet should persist. Its absence is further evidence against nonrandom chain configuration.

If, however, a doublet is observed in the ^{1}H NMR of the *n*-alkanes because the ends are differently solvated than the center, all aspects of the phenomenon can be rationalized. The chain ends experience, on the average, a slightly different magnetic environment than the center of the chain because the detailed nature of the solvation interaction affects the degree of shielding and deshielding due to the 1-chloronaphthalene. The presence of a bulky aromatic chromophore at one end of the chain leads to differential solvation of the two ends. The induced chemical shifts differ at the two ends, and as in **1**-18, a more complicated splitting is observed. The critical length for observing the doublet depends, of course, on the number of carbons at each end considered to be solvated differently than the chain interior. If the terminal CH_3 and four CH_2 groups experience the solvation effects associated with the chain ends, then a 10-carbon chain will show negligible splitting and a 16-carbon chain would have four CH_2 groups differently solvated. The ^{13}C chemical shift data are consistent with this explanation. Since the carbons of the alkyl chain will not be in as close proximity to the solvent as the alkyl hydrogens, ring current effects should be smaller for the carbons, consistent with the very small solvent shifts shown in Table II. Slightly larger solvent shifts are noted for the carbons close to the aromatic chromophore in **1**-18, consistent with the differential solvation inferred from the ^{1}H chemical shifts.

Thus it appears that all of our data and that of previous workers[1-4,6] can be accounted for in terms of (relatively small) differences in solvation of alkyl chain ends and chain interiors in aromatic solvents. It is unnecessary to invoke either severely folded alkane conformations or severely restricted rotation about individual bonds in aromatic solvents.

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Cross-Linking of Polymers with a Primary Size Distribution

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ABSTRACT: A univariate Stockmayer distribution has been obtained for the condensation of polymer chains with an initial size distribution. The technique involves the use of the theory of cascade processes. The final molecular size distribution is shown to be a compound distribution. The expression for weight average size is in agreement with Stockmayer. Initial weight average and distribution can be recovered from this distribution. In the special case of the compound Borel–Poisson distribution, multimodality can be detected.

There are at least three general theories dealing with polymer size distributions in the condensation of polymer chains with an arbitrary initial size distribution: The first, formulated by Stockmayer,[2] is based on Flory's theory[3] of condensation and follows a classical combinatorial argument. The second one, proposed by Charlesby,[4] uses distribution moments and moment ratios to describe gelation. The third theory is given by Saito,[5] who used a continuous size distribution and a phenomenological kinetic argument. These theories arrive at the same number average and slightly different expressions for the weight averages, but their distributions differ to a considerable extent.

Among these theories, the Stockmayer distribution is multivariate.[2] It is originated from the Flory–Stockmayer distribution for the condensation of polyfunctional mo-

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nomers of uniform size (eq 5 below). A multivariate distribution is seldom used in practical applications such as characterization by gel permeation chromatography (GPC).[6,7] However, since the basic Flory–Stockmayer distribution has been derived and reaffirmed rigorously by various probabilistic approaches,[8–11] the multivariate Stockmayer distribution for arbitrary chain size appears to be valid also.

Obviously a univariate size distribution is of great interest both theoretically and experimentally. In this paper, an attempt is made to reduce the Stockmayer distribution to a univariate version that can be used directly for the characterization of branched polymers.

Our terminology follows Stockmayer's in that "chains" are referred to as primary polymers and "molecules" are used to describe aggregates formed after cross-linking.[2] The technique adopted here is the probability generating function (pgf) approach of the cascade theory, which has been used successfully to derive size distributions and average properties of polymers obtained by the condensation of polyfunctional monomers of uniform size.[8,9] Although attempts have been made to extend this approach to the condensation of polydispersed chains,[9,10] the distributions generated are found to be either unsatisfactory or inconvenient in applications. This is probably due to the fact that size distributions have not been a major concern in these extended cascade treatments.

We are concerned mainly with the distribution aspect in the cascade theory, which will be subject to a slight modification to account for the initial chain size distribution. For this modification, we need to outline briefly the cascade theory and introduce its formalism. This is done in the next section. In the Average Sizes section we summarize the expressions of average sizes given by various theories. The modification of the cascade theory is given in the General Size Distribution section. This yields a general size distribution in the form of a pgf. A simple special case will be used to illustrate the curve shape of the resultant distribution (Applications).

Assumptions and Background

Most of the theories of branched polymers are based on the assumptions (a) that all functional groups are equally reactive and (b) that intramolecular reaction (cyclization) is excluded. Before gelation, both number and weight distributions are assumed to exist. In this paper we will retain these assumptions and use mainly a normalized weight distribution, which is identified as the weight fraction of an x-mer, a molecule with degree of polymerization (DP) = x.

The cascade theory,[8,9] in particular, considers the x-mer as a "tree". The "root" of this tree is formed by randomly choosing a monomeric unit of the type RA_n, where n is the number of functional groups. The root is also the "zero generation" in a given tree. The pgf of the number of functional groups in this generation is

$$F_0(u) = (1 - \alpha + \alpha u)^n \tag{1}$$

where α is the branching probability or the fraction of reacted functional groups, and u is an auxiliary variable related to the generating variable θ by

$$u = \theta F_1(u) \qquad 0 \le \theta \le 1, \qquad 0 \le u \le 1 \tag{2}$$

where $F_1(u)$ is the pgf of the first, second, . . . generations, or

$$F_1(u) = F_2(u) = \ldots = (1 - \alpha + \alpha u)^{n-1} \tag{3}$$

For a chemical condensation, the weight distribution $w(x)$ thus obtained is given by its pgf $W(\theta)$:

$$W(\theta) = \sum_x w(x)\theta^x = \theta F_0(u) \tag{4}$$

It is inherent in the cascade theory that $u(\theta)$ is a pgf, because $u(1) = 1$. It is also a generating variable for the functional groups in various generations. Clearly, $1 - \alpha + \alpha u$ is the pgf of a Bernoulli trial, which describes the chance of "success" as α and that of "failure" as $1 - \alpha$. The weight distribution thus generated is the well-known Flory–Stockmayer distribution:[2,3,8–11]

$$w(x) = \frac{n}{(n-1)x+1}\binom{(n-1)x+1}{x-1}\alpha^{x-1}(1-\alpha)^{(n-2)x+2} \qquad x \ge 1 \tag{5}$$

which has a number average

$$1/\bar{x} = \sum_x \frac{1}{x} w(x) = 1 - n\alpha/2 \tag{6}$$

and a weight average

$$\bar{x}_w = \sum_x x w(x) = (1 + \alpha)/[1 - (n - 1)\alpha] \tag{7}$$

Recently this distribution has been identified as one of the Lagrange distributions as well as a power series distribution.[11] In the Lagrange distribution treatment, $F_1(u)$ is called the transformer pgf.[12] When $n >> 1$, $\alpha \rightarrow 0$ such that $n\alpha \rightarrow \gamma$, eq 5 becomes

$$w(x) = x^{x-1}(\gamma e^{-\gamma})^x/\gamma x! = B(x;\gamma) \tag{8}$$

where γ is the cross-linking index.[2] This form is called the Borel distribution in statistics,[12,13] abbreviated here as $B(x;\gamma)$. Using a discrete version of Saito's treatment, a weighted Borel distribution also results.[5b]

Gordon[9] extended the cascade theory to the condensation of preformed polymers with an initial weight distribution $f(y)$. Assuming each repeating unit bears a functional group of a given kind:

$$F_0(u) = \sum_y f(y)(1 - \alpha + \alpha u)^y \tag{9}$$

$$F_1(u) = \sum_y f(y)(1 - \alpha + \alpha u)^{y-1} \tag{10}$$

The weight distribution pgf is again expressed by eq 4. However, the "monomer" that forms the root of the tree is an arbitrary chain.

To visualize the distribution aspect of this formulation, consider a primary distribution of the Poisson type

$$f(y) = e^{-\lambda}\frac{\lambda^{y-1}}{(y-1)!} = p(y;\lambda) \tag{11}$$

which gives the weight fraction of a y-mer in the primary chains. The corresponding pgf is

$$\phi(\theta) = \sum_y f(y)\theta^y = \theta \exp[\lambda(\theta - 1)] \tag{12}$$

It follows that for this Poisson distribution

$$W(\theta) = u(1 - \alpha + \alpha u) \tag{13}$$

$$\theta = u/F_1(u) = u/\exp[\lambda\alpha(u - 1)] \tag{14}$$

The weight distribution of the cross-linked molecules can be shown to be

$$\begin{aligned} w(x) &= \text{coefficient of } \theta^x \text{ in } W(\theta) = (1/x) \times \\ &\quad [\text{coefficient of } u^{x-1} \text{ in } W'(u)[F_1(u)]^x] = \\ &\quad [1 - \alpha + 2(x - 1)/\lambda x]B(x;\lambda\alpha) \end{aligned} \tag{15}$$

where we have used Good's theorem of Lagrange expansion to invert $W(\theta)$.[8] In eq 15, x is the number of primary chains in the moleule.

The distribution in eq 15, like the Flory–Stockmayer and the Borel distributions, is very broad and highly skewed.

Table I
Calculated Distributions at $\gamma = 1$

	$w(x)$		
x	Flory–Stockmayer, eq 5	Borel, eq 8	eq 15
1	0.3376	0.3679	0.3475
2	0.1348	0.1353	0.1353
3	0.0766	0.0747	0.0761
4	0.0508	0.0488	0.0502
5	0.0368	0.0351	0.0363
10	0.0133	0.0125	0.0131
20	0.0048	0.0044	0.0046

All of these distributions have a mode at $x = 1$. These properties are shown in a sample calculation in Table I, by assuming $n = 19$ in eq 5, $\lambda = 18$ in eq 15, and $\gamma = 1$ (the gel point) in all cases.

The limitation of this treatment is reflected in the extreme case at which $\alpha = 0$, i.e., no cross-linking has yet taken place. At this limit $W(\theta) = \theta$, which obviously fails to recover the initial Poisson distribution. Another test of this treatment is done by considering the weight average in eq 15

$$\bar{x}_w = (1 + \alpha)/(1 - \lambda\alpha) \tag{16}$$

which at $\alpha = 0$ reduces to $\bar{x}_w = 1$ but not $\lambda + 1$ as should be obtained from the Poisson distribution. The inadequacy of this extended treatment is inherent in the original assertion that a "monomeric" unit is itself a variable. To apply the cascade theory to a practical situation in which the final molecular size is expressed directly as the number of repeating units, a modification of this formulation is necessary.

Average Sizes

For reasons given above, our first step is to examine a distribution by considering its first two moments, or correspondingly, its number and weight averages. For the condensation of uniform chains, the discrete distribution functions appropriate for polymers are of the form of power series distributions.[11] This means that the single-parameter expressions of the two average sizes are sufficient to generate a univariate distribution.[11,13] For the condensation of polydispersed chains, unfortunately, the final size distribution may not be a power series distribution. However, it still can be assumed that correct expressions of the two averages are a prerequisite of a valid distribution function.

For the number average, various authors arrived at the same expression[2,4,5]

$$\bar{x} = \bar{y}/(1 - \bar{y}\alpha/2) \tag{17}$$

where $\bar{y}$ is the number average size of the primary chains. This expression is unequivocal because it can be deduced from a simple stoichiometry consideration and the definition of α.

From his multivariate distribution Stockmayer derived the weight average as

$$\bar{x}_w = \bar{y}_w(1 + \alpha)/[1 - (\bar{y}_w - 1)\alpha] \tag{18a}$$

whereas Charlesby[4] arrived, in our notation, at

$$\bar{x}_w = \bar{y}_w/(1 - \bar{y}_w\alpha) \tag{18b}$$

The long-chain approximation given by Stockmayer also has the form of eq 18b.[2] In these equations, $\bar{y}_w$ is the weight average size of the primary chains.

All these average expressions give the correct initial averages at $\alpha = 0$. In comparing these equations with eq 16, we note that a factor $\bar{y}_w$ is missing in the extended cascade theory formulation

Further extension of the cascade theory has been made by Kajiwara and Ribeiro.[10] Taking the initial chain with DP = y into account but without referring to the intermediate step of $F_0(u)$ and $F_1(u)$, these authors write

$$u = \sum_y f(y)\theta^y(1 - \alpha + \alpha u)^{y-1}$$

$$W(\theta) = \sum_y f(y)\theta^y(1 - \alpha + \alpha u)^y$$

In our notation these summations can be reduced to

$$u = \phi(\theta(1 - \alpha + \alpha u))/(1 - \alpha + \alpha u) \tag{19}$$

$$W(\theta) = \phi(\theta(1 - \alpha + \alpha u)) \tag{20}$$

Here $\phi(\ )$ is a functional, i.e., a "function of a function". On evaluating $\bar{x}_w = W'(1)$, it can be shown that this formulation recovers the missing factor $\bar{y}_w$ to yield the correct average in eq 18a. It also recovers the initial chain size distribution, i.e., $W(\theta) = \phi(\theta)$ at $\alpha = 0$.

Kajiwara and Ribeiro did not attempt to generate the final size distribution. We have made this attempt but found that the pgf's in eq 19 and 20 do not provide sufficient information to give a univariate distribution (see below). In the following section we offer another modification to the cascade theory by a simple randomization argument. It will be shown that the information required to generate the final size distribution is provided by the initial chain size distribution.

General Size Distribution

Our treatment retains Gordon's formulation up to eq 9 and 10. Before introducing the initial size distribution, we first note that $F_0(u)$ and $F_1(u)$ are actually the pgf's of conditional probabilities. *Conditional* on given n groups, or a unit of the type RA_n in the zero generation, the expressions for $F_0(u)$ and $F_1(u)$ are given by eq 1 and 3. For polydispersed chains, the fixed number n is replaced with random variable y; the generalized or unconditional pgf's can then be expressed by eq 9 and 10, as obtained by Gordon.[9]

With our notation of functionals, these equations become

$$F_0(u) = \phi(1 - \alpha + \alpha u)$$

$$F_1(u) = \phi(1 - \alpha + \alpha u)/(1 - \alpha + \alpha u)$$

The pgf $W(\theta)$ is still given by eq 4. Therefore, we write

$$u = \theta F_1(u) = \theta\phi(1 - \alpha + \alpha u)/(1 - \alpha + \alpha u) \tag{21}$$

$$W(\theta) = \theta F_0(u) = \theta\phi(1 - \alpha + \alpha u) \tag{22}$$

These two equations have also been obtained by Gordon,[9] though not in the form of functionals.

As indicated above, the pgf's in eq 21 and 22 give the distribution in terms of chains with arbitrary length. To express the final distribution directly in terms of repeating units, the chain size should be randomized. In standard statistical techniques this is done by replacing the variable θ in the above equations with $\phi(\theta)$[13]

$$u(\phi) = \phi\phi(1 - \alpha + \alpha u(\phi))/[1 - \alpha + \alpha u(\phi)] \tag{23}$$

$$W(\theta) = \phi\phi(1 - \alpha + \alpha u(\phi)) = u(\phi)[1 - \alpha + \alpha u(\phi)] \tag{24}$$

where we have abbreviated $\phi(\theta)$ as ϕ. Furthermore, let $\phi'(\theta) = \mathrm{d}\phi(\theta)/\mathrm{d}\theta$ and noting $\phi'(1) = \bar{y}_w$, $u(1) = \phi(1) = 1$ at $\theta = 1$, we obtain from eq 23

$$\left(\frac{\mathrm{d}u(\phi)}{\mathrm{d}\phi}\right)_{\phi=1} = [1 - (\bar{y}_w - 1)\alpha]^{-1} \tag{25}$$

From eq 24 we have

$$\bar{x}_w = W'(1) = (1+\alpha)\bar{y}_w\left(\frac{\mathrm{d}u(\phi)}{\mathrm{d}\phi}\right)_{\phi=1} = \bar{y}_w(1+\alpha)/[1-(\bar{y}_w-1)\alpha]$$

in agreement with Stockmayer.[2] Therefore, eq 24 generates a univariate Stockmayer distribution which has the form of a compound distribution.[13]

The conversion between $u(\theta)$ and θ is still given by eq 21. It should be noted that at $\alpha = 0$, eq 24 reduces to $W(\theta) = \phi(\theta)$; i.e., the initial distribution is recovered.

We will call the distribution generated by eq 21 and 22 the "branching" distribution. This is the distribution obtained by using Gordon's formulation. Examples have already been listed in Table I. Branching distributions are characterized as being highly dispersed. In the terminology of compound distributions,[13] the branching distribution is a compounding distribution, with the chain size distribution as the distribution being compounded.

It is interesting to note that a similar technique has been used in the "coupling" of preformed linear polymers, although no pgf or compounding have been recognized.[14,15] Without using a pgf formulation, the treatment in coupling has been extensive and tedious.

We also note that in all of the distributions discussed above the pgf $W(\theta)$ always maintains the form given by eq 13 or 24. The only thing that varies is the form of u. This form of $W(\theta)$ may have potential applications since $W(1)$ is the weight fraction of the sol after gelation.[8]

Applications

As an example of applications, consider again the Poisson distribution in eq 11. From eq 21, we obtain the transformation relation

$$u = \theta \exp[\lambda\alpha(u-1)] \tag{26}$$

which indicates that $u(\theta)$ is the pgf of the Borel distribution $B(x;\lambda\alpha)$.[11] The invariant form of the pgf of final distribution can be written as

$$W(\theta) = (1-\alpha)u(\phi) + \alpha u^2(\phi) \tag{27}$$

This equation indicates that a fraction $1-\alpha$ of the molecules follows a compound Borel distribution; another fraction α follows a self-convoluted compound Borel distribution. If the Poisson distribution is not compounded (i.e., the "monomers" are not randomized), the final distribution is given by eq 15.

From Table I we see that all three "branching" distributions have a similar feature. If the primary chains are long, and before gelation occurs, α is very small. Therefore, as a first order of approximation we can use the Borel distribution as the compounding distribution. Thus, eq 27 is simplified to

$$W(\theta) = u(\phi) \tag{28}$$

Equations 26 and 28 generate the Borel–Poisson distribution.

The property of this distribution is schematically illustrated in Figure 1. The upper part of this figure is the Borel distribution; the lower part of the figure is the compound distribution. The randomization of "monomers" is clearly demonstrated here: the "sticks" in the Borel distribution are replaced with the narrow Poisson curves. The dashed "envelopes" of both distributions maintain the feature of the Borel distribution. In Figure 1b the largest peak corresponds to the initial chains with average size λ. This peak is obtained by randomizing the mode $x = 1$ in Figure 1a. The second, third, . . . peaks appear approximately at 2λ, 3λ, . . ., respectively. These peaks are actually describing the condensation process, i.e., the "monomeric" chains are cross-linked to form "dimers," "trimers," . . ., etc.[6]

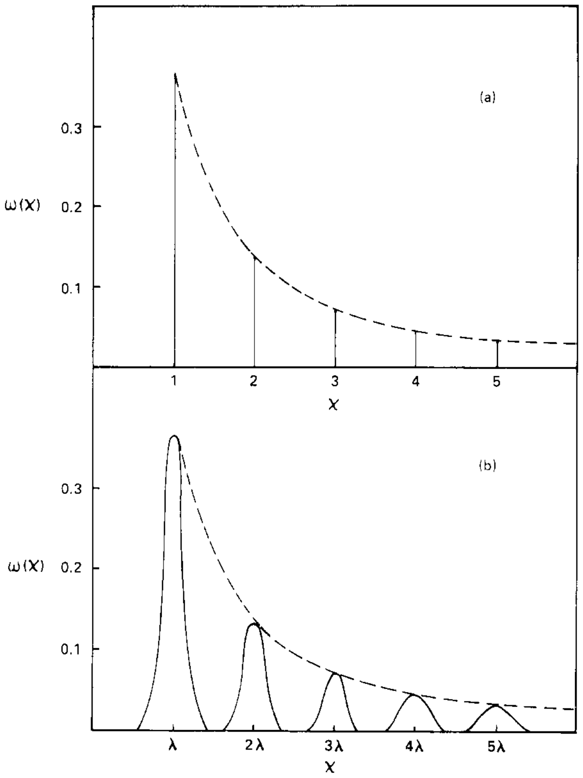

Figure 1. Randomization of "monomers" in the Borel distribution. (a) Borel distribution for the condensation of uniform chains. (b) Borel–Poisson distribution for the condensation of primary chains with a Poisson distribution.

The Borel–Poisson distribution can be better appreciated by writing the distribution explicitly

$$w(x) = B(1;\gamma)p(x;\lambda) + B(2;\gamma)p(x;2\lambda) + \ldots \tag{29a}$$

$$w(x) = \sum_{n=1}^{\infty} B(n;\gamma)p(x;n\lambda) \tag{29b}$$

where the first, second, . . . terms in eq 29a give the weight fractions of the "monomers", "dimers", . . ., respectively. From this argument and Figure 1, we can readily see that the Borel–Poisson distribution shows multi-modality.

In general, multi-modality can be detected when the initial chain length distribution is sufficiently narrow. Because of the mode in a branching distribution (eq 5, 8, or 15), the largest mode in the resultant compound distribution always represents the "monomeric" chains. If the initial chain length distribution is broad, the compound distribution maintains the broad feature but multi-modality may not be observed. These conclusions are in agreement with Kells and Guillet[6] and Schultz,[7] who use Saito's approach.

Results of calculating the Borel–Poisson distribution using λ = 20 and two values of γ are shown in Figure 2. There is an increase in the visibility of multiple peaks as γ goes from 0.3 to 0.6. Multi-modal distributions of branched polymers have been observed in GPC and sedimentation measurements.[16] Theoretical calculations using Saito's continuous distribution function have also been carried out.[6,7] The calculated results also confirm the existence of multiple peaks.

The accuracy in our calculation can be improved by using eq 27 instead of its approximation, eq 28. In the case of the Borel distribution, the second term in eq 27 involves

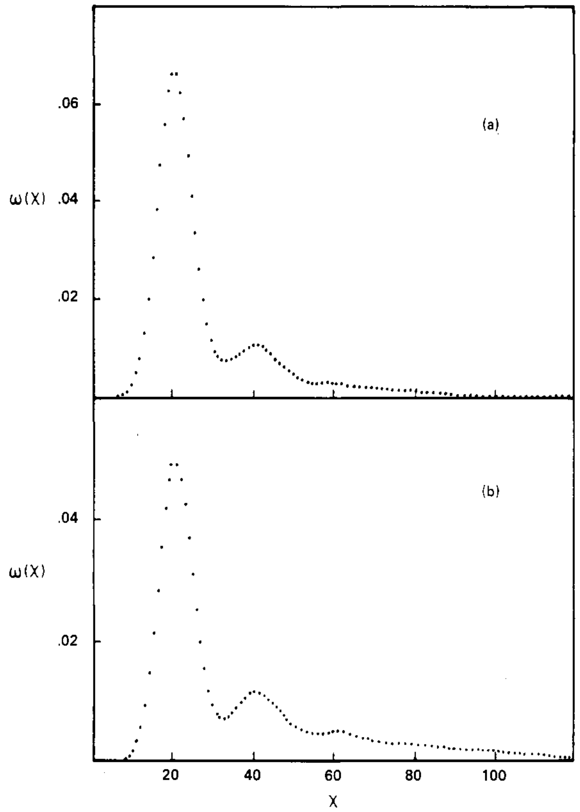

Figure 2. Calculated Borel–Poisson distribution with $\lambda = 20$: (a) $\gamma = 0.3$, (b) $\gamma = 0.6$.

the square of eq 26 as the pgf. Since this self-convoluted Borel distribution is a special case of the Borel–Tanner distribution,[12,13] calculation of the resultant compound distribution does not present additional complexity. For short-chain branching, accuracy can be further improved by using the Flory–Stockmayer distribution, instead of the Borel, as the compounding distribution.

The approximation used in eq 28 and Figure 2 overestimates the first peak area. Including a convoluted term in eq 27 increases the areas of the second and later peaks, at the expense of the first. However, in the example given for $\lambda = 20$ this increased visibility of the second peak is not significant.

At this point it is appropriate to examine the distribution generated by the formulas of Kajiwara and Ribeiro, eq 19 and 20. Again using the Poisson example, eq 11, we obtain

$$u = \theta \exp\{\lambda[\theta(1 - \alpha + \alpha u)] - 1\} \qquad (30)$$

which has the form of a compound Poisson distribution.[13] The distribution being compounded has a pgf $\theta(1 - \alpha + \alpha u)$ which remains indeterminate. If the approximation in eq 28 is adopted here, i.e., $\theta(1 - \alpha + \alpha u) \sim \theta$, then eq 30 reduces to the simple Poisson form, eq 12. Combining eq 19 and 20 the general form of $W(\theta)$ in eq 13 still applies. The same approximation also reduces $W(\theta)$ to the Poisson form. Therefore, this approximation amounts to the regeneration of the initial distribution, and there is no longer any compounding as a result of making this approximation.

We note that when this approximation is used in eq 28 it is a good one for large values of λ. Furthermore, as indicated above, the final distribution can be calculated with or without this approximation. When it is used for u, as in the cases of eq 19 or 21, the transformation reduces prematurely to the initial pgf. Since the form of the transformer pgf is so sensitive to this approximation, it is obvious that this approximation should not be used for u, although its use in W is justifiable.

Unfortunately, without this approximation the Kajiwara–Ribeiro formulation does not provide sufficient information for the distribution being compounded. In the example of eq 30 the compounding distribution is Poisson, which is no longer a branching distribution. Therefore, we conclude that this formulation is unsatisfactory as far as the size distribution is concerned.

Conclusions

A simple randomization of "monomers" accounts satisfactorily for many important features in the condensation of polydispersed chains. The corresponding statistical technique is the compounding of a primary distribution with a branching distribution.

This technique has been shown to be capable of detecting multi-modality in the distribution curve, in agreement with experiments[16] and previous calculations.[6,7] Without using a pgf formalism, a similar technique has been applied to the coupling of linear polymers.[14,15] If a Poisson type prepolymer is coupled, multi-modality also appears.[14] In our terminology, this coupling results in a negative binomial-Poisson distribution.

Recent developments in statistical distributions[11,13] have provided polymer chemists with a powerful tool in molecular size distributions. We have already demonstrated this power with the applications of the Lagrange, power series,[11] and compound distributions.

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