Theory of Molecular Size Distribution and Gel Formation in Branched Polymers II. General Cross Linking

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Theory of Molecular Size Distribution and Gel Formation in Branched Polymers

II. General Cross Linking *

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A statistical calculation of the gel point and of the molecular size distribution is made for cross-linked high polymers of arbitrary initial size distribution. The weight-average polymerization degree of the cross-linked polymer depends only on the weight-average polymerization degree of the initial polymer and the degree of cross linking. The results obtained also apply to certain vinyl-divinyl copolymers. Polymerization degrees can be estimated from observations of the gel point.

1. INTRODUCTION

IT is well known and practically important that, when sufficiently frequent branching or cross linking of chains occurs during the course of a polymerization or polycondensation reaction, the enhanced capacity for further growth of the larger molecules (due to their larger number of unreacted end groups) leads ultimately to the formation of a few network structures so huge that the material changes rather abruptly from a fluid to a gel. The statistical theory of such reactions, developed by Flory[1-4] and embellished by the writer,[5] has had conspicuous success in predicting the gel point[1] for the several polycondensations to which it has been applied. In this paper the theory is extended to a more general case than those previously considered; namely, the cross linking of a system of chains with *arbitrary* initial size distribution. The rather formidable size distribution equations which are obtained lead to relatively simple expressions for the gel point and the several average polymerization degrees. It transpires that these equations should also apply to some vinyl-divinyl copolymers, if certain plausible assumptions are made.

[1] P. J. Flory, J. Am. Chem. Soc. 63, 3083 (1941).
[2] P. J. Flory, J. Am. Chem. Soc. 63, 3091 (1941).
[3] P. J. Flory, J. Am. Chem. Soc. 63, 3096 (1941).
[4] P. J. Flory, J. Phys. Chem. 46, 132 (1942).
[5] W. H. Stockmayer, J. Chem. Phys. 11, 45 (1943), hereinafter called I.

2. THE GEL POINT

The polymeric molecules of various sizes which initially comprise the system will be called *chains*, although they need not necessarily be linear. In the simplest case, each monomer unit in a chain bears one functional group which can be linked through chemical reaction to others of its kind, either with or without the aid of an added cross-linking agent.[6] All functional groups are assumed to be similar and of the same reactivity. The term *molecule* will be reserved for the aggregates which exist after some cross linking has taken place; a molecule therefore consists of one or more chains. Let the system contain N_1 monomeric chains, N_2 dimeric chains, ————, N_s s-meric chains, — etc. The number-average size (polymerization degree) of the chains is thus

$$\lambda_n = \sum s N_s / \sum N_s, \qquad (1)$$

and the weight-average size is

$$\lambda_w = \sum s^2 N_s / \sum s N_s = \sum s w_s, \qquad (2)$$

where w_s, the weight fraction of s-meric chains, is given by

$$w_s = s N_s / \sum s N_s. \qquad (3)$$

Since each monomeric unit bears one functional group, w_s is also the fraction of groups residing on s-meric chains.

It will be assumed (as in the previous papers[1-5]) that when cross linking occurs no rings can form; that is, any two chains can be cross linked to

[6] Vulcanization processes are obviously of this type. For several other examples, see B. S. Garvey, Jr., C. H. Alexander, F. E. Küng, and D. E. Henderson, Ind. Eng. Chem. 33, 1060 (1941).

each other at only one point. This assumption introduces only a moderate error in undiluted systems, at least up to the gel point. Then when a fraction α of the functional groups in the system has become involved in cross links, the number of molecules M is equal to the number of chains less the number of linkages, or

$$M = \sum N_s - (\alpha/2)\sum s N_s$$
$$= \sum N_s (1 - \alpha\lambda_n/2).$$
(4)

The quantity $\gamma \equiv \alpha\lambda_n$ is the (number) average number of cross-linked units per chain, and was called by Flory[3] the *cross-linking index*.

A simple procedure[1] suffices for the prediction of the gel point. Consider a particular cross-linked group attached to some chain chosen at random from the system. The probability that the reacted group at the other end of the cross link is on an s-meric chain is w_s. Since this second chain carries s groups in all, and since the probability that a group has formed a cross link is α, the expected number of *additional* chains to which this second chain is connected is $\alpha(s-1)$. Therefore the average expectance of additional chains ν (averaged over all possible chain sizes) is

$$\nu = \sum_s w_s \alpha(s-1) = \alpha(\lambda_w - 1).$$
(5)

If ν exceeds unity, there is a finite probability that a chain chosen at random from the system belongs to an "infinitely large" molecule.[1] Hence the critical value of α for the appearance of such large molecules, physically identified with the gel point, is

$$\alpha_c = (\lambda_w - 1)^{-1}.$$
(6)

If the initial material is a fairly high polymer, so that $\lambda_w \gg 1$, the critical value of the cross-linking index is

$$\gamma_c \equiv \alpha_c\lambda_n \simeq \lambda_n/\lambda_w.$$
(7)

If all chains are of equal length, $\lambda_n = \lambda_w$ and $\gamma_c = 1$, as previously found by Flory.[3] The great heterogeneity of the molecular size distribution at the gel point is illustrated by the value of the number-average number of chains per molecule, which equals

$$\sum N_s/M = (1-\gamma/2)^{-1},$$
(8)

from Eq. (4). For most synthetic linear polymers, λ_w/λ_n lies between 1.5 and 2, so that when such substances are cross linked $\sum N_s/M$ is only

about 4/3 to 3/2 at the gel point, although some extremely large molecules are present.

We wish also to consider the case of a copolymer, in which only a fraction ρ of the monomeric units contained in the chains bears functional groups susceptible to the cross-linking reaction. If N_{sl} represents the number of s-meric chains carrying l reactive groups each, the fraction of the reactive groups borne by chains carrying l such groups each is

$$f_l = \sum_s l N_{sl}/\sum_s \sum_l l N_{sl}, \quad (s \geq l \geq 1).$$
(9)

Repeating the previous argument, we now find the average expectance of additional chains to be

$$\nu = \sum_l f_l \alpha(l-1)$$
$$= \alpha\sum_s \sum_l l(l-1)N_{sl}/\sum_s \sum_l l N_{sl}.$$
(10)

The general evaluation of this expression demands an explicit formula for N_{sl}. If the reactive units are distributed *at random* throughout all the chains ("true copolymer"),[7] we may write

$$N_{sl} = N_s \binom{s}{l} \rho^l (1-\rho)^{s-l},$$
(11)

where N_s is the total number of s-meric chains of all compositions. In this case the sums are easily found, with the result

$$\nu = \alpha\rho(\lambda_w - 1),$$
(12)

so that the gel point is now given by

$$\alpha_c = [\rho(\lambda_w - 1)]^{-1},$$
(13)

as reported in a recent note.[8] Since the cross-linking index is now given by $\gamma = \alpha\rho\lambda_n$, its critical value is still (for long chains) equal to λ_n/λ_w as expressed in Eq. (7).

For other than random copolymers, Eqs. (12) and (13) will in general not be correct. They may be formally retained by altering the significance of ρ to that of an unknown parameter which approaches the actual average composition of the chains in the case of a true copolymer. In general, this redefined ρ may vary with the extent of polymerization as well as with the average composition. It appears, however, that in some cases

[7] F. T. Wall, J. Am. Chem. Soc. **63**, 1862 (1941).
[8] W. H. Stockmayer and H. Jacobson, J. Chem. Phys. **11**, 393 (1943).

such variation can be rather small.[9] It is probably safe to expect that ρ will be approximated fairly well by the average composition if the chains have been formed by a single batch copolymerization. If, however, the chains are mechanical mixtures of rather different copolymers, such an approximation will be poor.

It has already been pointed out[8] that in cases where Eq. (13) holds it is possible in principle to determine λ_w experimentally by observations of the gel point. Thus the weight-average polymerization degree of polyvinyl acetate, for example, could be obtained by measuring the extent of its ester interchange with diethyl phthalate at gelation.[6]

3. MOLECULAR SIZE DISTRIBUTION

In this section the methods developed in I[5] are employed to derive the actual distribution of molecular sizes up to the gel point. To avoid excessively cumbersome equations, the detailed treatment is restricted to the case that all units in the chains carry a reactive group ($\rho = 1$).

The description of any single molecule requires specification of the number of chains of each size which it contains. We denote by n_1, n_2, n_3, $\cdots n_s$, etc., these numbers of chains, and for brevity represent any particular set of these numbers by the symbol $\{n_s\}$. The symbol $m\{n_s\}$ will be used for the number of molecules described by a particular set $\{n_s\}$. The most probable molecular size distribution is then written (cf. I)

$$m\{n_s\} = A\omega\{n_s\}\prod_s (\xi_s^{n_s}/n_s!),\qquad (14)$$

where A and all the ξ_s are Lagrangian multipliers to be evaluated subsequently, and $\omega\{n_s\}$ is the number of different ways in which a molecule described by $\{n_s\}$ can be constructed from its constituent chains. Generalization of the argument of I (Appendix A) gives the result

$$\omega\{n_s\} = \frac{(\sum sn_s - \sum n_s)!}{(\sum sn_s - 2\sum n_s + 2)!}\prod_s s^{n_s}.\qquad (15)$$

Now the Lagrangian multipliers must be so chosen that

$$M = \sum_{\text{all }\{n_s\}} m\{n_s\},\qquad (16)$$

[9] C. S. Marvel and G. L. Schertz, J. Am. Chem. Soc. 65, 2054 (1943).

and

$$N_t = \sum_{\text{all }\{n_s\}} n_t m\{n_s\}, \text{ for all } t.\qquad (17)$$

The sums go over all possible sets $\{n_s\}$, and M is given by Eq. (4). In the simpler cases treated in I, the prototypes of Eqs. (16) and (17) required summations which were relatively easy to perform directly; here an heuristic attack is of advantage. Experience with the simpler cases suggests the substitutions

$$s\xi_s = w_s\alpha(1-\alpha)^{s-2},\qquad (18)$$

$$A = (\sum sN_s)(1-\alpha)^2/\alpha.\qquad (19)$$

It is shown in the Appendix that this choice does satisfy Eqs. (16) and (17). The distribution law, obtained by substituting Eqs. (15), (18), and (19) into Eq. (14), is thus

$$m\{n_s\} = (\sum sN_s)\frac{(\sum sn_s - \sum n_s)!}{(\sum sn_s - 2\sum n_s + 2)!}\alpha^{\sum n_s - 1}$$

$$\times (1-\alpha)^{\sum sn_s - 2\sum n_s + 2}\prod_s (w_s^{n_s}/n_s!).\quad (20)$$

This law may be employed to derive the weight-average molecular size $\bar{P}_w$ of the cross-linked polymer. A molecule contains $\sum sn_s$ units in all, so that the weight fraction of molecules described by $\{n_s\}$ is simply

$$W\{n_s\} = (\sum sn_s)m\{n_s\}/(\sum sN_s).\qquad (21)$$

Then the weight-average molecular size is

$$\bar{P}_w = \sum_{\text{all }\{n_s\}} (\sum sn_s)W\{n_s\}.\qquad (22)$$

As shown in the Appendix, carrying out the summation yields the result

$$\bar{P}_w = \lambda_w(1+\alpha)/[1-\alpha(\lambda_w-1)].\qquad (23)$$

Since this equation requires $\bar{P}_w$ to become infinite at $\alpha_c = (\lambda_w-1)^{-1}$, indicating the presence of some very large molecules, Eq. (23) may be regarded as furnishing an independent derivation of Eq. (6).

It is apparent that in the special case that all chains have the same size s, Eq. (20) reduces to

$$m_n = sN\alpha^{n-1}(1-\alpha)^{sn-2n+2}\frac{(sn-n)!}{n!(sn-2n+2)!},\qquad (24)$$

which was derived in I. If, in addition, $s \gg 1$, use

of the Stirling formula leads to the following expression for the weight fractions:

$$W_n = n^{n-1}(\gamma e^{-\gamma})^n / n! \gamma, \qquad (25)$$

where γ, equal to $s\alpha$, is the cross-linking index. The above equation was derived by Flory[3] by methods appropriate to this special case.

The molecular size distribution for the case $\rho < 1$ (cf. Section 2) could in principle be found by straightforward extension of the methods described above. It is sufficient to remark here that for a "true copolymer" the formulae for the average molecular sizes carry over if α is replaced everywhere by $\alpha\rho$. If the chains are long, the average sizes are given by the simple expressions

$$\bar{P}_n = \lambda_n / (1 - \gamma/2), \qquad (26)$$

$$\bar{P}_w = \lambda_w / (1 - \gamma/\gamma_c), \qquad (27)$$

with $\gamma = \alpha\rho\lambda_n$ and $\gamma_c = \lambda_n/\lambda_w$. Formally these equations may be retained for other than random copolymers by substitution of an appropriate parameter in place of ρ, but as stated previously, such maneuvers require considerable understanding of the copolymerization reaction.

The foregoing results are unfortunately of little aid in characterizing materials for which the cross-linking reaction has progressed beyond the gel point. Here the inclusion of ring formation is essential. The treatment employed by Flory[3] (which is probably a fair approximation) shows in any case that the residual fraction of relatively small molecules (the extractable "sol fraction") bec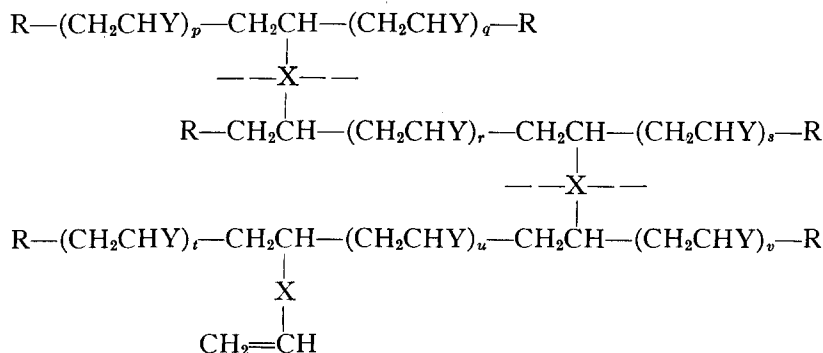omes negligible if the reaction proceeds much beyond the gel point. For interpreting the physical properties (such as rubber-like elasticity) of these materials the "number of molecules" has little significance; what is required is the number and size distribution of the chain portions lying between cross links.[10, 11]

4. VINYL-DIVINYL COPOLYMERS

The copolymerization of a vinyl derivative with sufficient quantity of a divinyl derivative also leads to gelled three-dimensional polymers,[6, 12, 13] but the mechanism differs from the cases we have treated above, in that polymerization and cross linking are concomitant rather than consecutive. It nevertheless appears that under certain conditions, which we shall discuss, the results just obtained may be applied to these systems.[8]

Some of the assumptions required are quite generally obeyed.[14] One of these is that at any instant the fraction of material involved in active growing chains is negligible compared to the amounts of stable polymer and residual monomer.

The stable polymer consists of *molecules*, which are subdivided for our purpose into *chains*. These chains may be most easily pictured as the aggregates which would remain if suddenly every doubly-reacted divinyl unit in the polymer were to be cut in half. If $CH_2 = CHY$ and $CH_2 = CH - X - CH = CH_2$ represent the two monomers, the molecule pictured below would consist of three chains.

$$R-(CH_2CHY)_p-CH_2CH-(CH_2CHY)_q-R$$
$$|$$
$$--X--$$
$$|$$
$$R-CH_2CH-(CH_2CHY)_r-CH_2CH-(CH_2CHY)_s-R$$
$$|$$
$$--X--$$
$$|$$
$$R-(CH_2CHY)_t-CH_2CH-(CH_2CHY)_u-CH_2CH-(CH_2CHY)_v-R$$
$$|$$
$$X$$
$$|$$
$$CH_2=CH$$

[10] H. M. James and E. Guth, J. Chem. Phys. 11, 455 (1943).
[11] P. J. Flory and J. Rehner, Jr., J. Chem. Phys. 11, 512 (1943).
[12] H. Staudinger and W. Heuer, Ber. 68, 1618 (1935).
[13] R. G. W. Norrish and E. F. Brookman, Proc. Roy. Soc. A163, 205 (1937).

[14] For recent concepts of the mechanism of addition polymerization, consult: J. Abere, G. Goldfinger, H. Mark, and H. Naidus, Ann. N. Y. Acad. Sci. 44, 267 (1943); C. C. Price, ibid. 44, 351 (1943); H. M. Hulburt, R. A. Harman, A. V. Tobolsky, and H. Eyring, ibid. 44, 371 (1943).

In this example, R represents fragments from a peroxide type catalyst,[14] and the cutting process described above would occur at the places indicated by dashed lines. With the above definition of a chain, it is not necessary to make special provision for any branching[15] which might result from chain-transfer processes, and which seems to occur to a small but noticeable extent in the polymerization of monovinyl derivatives. If such branching takes place, the "chains" will not all be topologically linear, but this fact in no way alters the statistical problem.

It is clear that, if all the double bonds located on divinyl units have the same probability of reaction α, then Eqs. (9) and (10) can be applied to the case at hand. Here N_{sl} is the number of stable polymer chains, consisting of s reacted double bonds in all, which contain l reacted double bonds attached to divinyl units. In order that α be an independent probability, the rates of all steps in the polymerization mechanism must be independent of the size of the molecules to which the reacting groups adhere. It has been demonstrated experimentally[16] that this situation obtains in polyesterification reactions. With regard to vinyl polymerization, Norrish and Smith[17] have suggested that the termination rate (which may be diffusion-controlled) decreases with an increase in chain length, at least for methyl methacrylate. It is difficult, however, to understand such a variation physically, in view of the well-known segment-flow behavior of flexible long chains.[18] An alternative explanation of the effects observed by Norrish and Smith is not improbable, and is to be preferred in the absence of further evidence. Herington and Robertson,[19] for example, find that the molecular size distribution of polystyrene[20] is in satisfactory accord with the assumption that the variation of reactivity with molecular size is insignificant.

[15] G. V. Schulz, Zeits. f. physik. Chemie **B44**, 227 (1939).
[16] P. J. Flory, J. Am. Chem. Soc. **61**, 3334 (1939).
[17] R. G. W. Norrish and R. R. Smith, Nature **150**, 336 (1942).
[18] W. Kauzmann and H. Eyring, J. Am. Chem. Soc. **62**, 3113 (1940).
[19] E. F. G. Herington and A. Robertson, Trans. Faraday Soc. **38**, 490 (1942).
[20] G. V. Schulz, A. Dinglinger, and E. Husemann, Zeits. f. physik. Chemie **B43**, 385 (1939).

With this assumption of equal reactivity, α becomes the reacted fraction of the double bonds attached to divinyl units, and could be found experimentally from the composition of the copolymer and the over-all reacted fraction of double bonds. The problem of evaluating the sums of Eq. (10) in the general case has already been discussed. In the special case of a "true copolymer," Eq. (13), and the distribution laws of Section 3, may be employed, with ρ equal to the composition of the original system (expressed as the over-all fraction of double bonds residing on divinyl units) and α equal to the over-all reacted fraction of double bonds. It should be noted that α is not identical with the weight fraction of polymer formed, since the polymer contains some unreacted double bonds (on divinyl units of which only one bond has reacted). The quantity λ_w is equal to the weight average number of (reacted) double bonds per chain.[21]

The ideal case just discussed might be realizable experimentally if the two monomers were judiciously chosen. An especially interesting situation would occur if the rates were independent of the composition ρ, for then λ_w in the copolymer would equal the weight average polymerization degree of a polymer prepared from the pure monovinyl reactant ($\rho = 0$) under identical conditions.[8]

Apparently no suitable experimental data on the gel point in vinyl-divinyl copolymerizations have yet been published.[22] The well-known case of styrene and p-divinylbenzene[12] is not described by Eq. (13), since the latter substance enters the polymer more readily than styrene. Qualitatively the agreement is satisfactory. If temperature and concentrations are such that λ_w is 2000, then 0.05 equivalent percent (about 0.03 weight percent) of divinyl-benzene is sufficient to produce an infusible polymer according to Eq. (13); the actual limit would be expected to be even lower.

The writer is grateful to Homer Jacobson for helpful discussion and criticism.

[21] If the termination process is a disproportionation of two radicals which leaves a double bond in one chain, or if a solvent takes part in chain transfer, slight modifications are required. At all significant degrees of polymerization, however, these effects are negligible.
[22] Experiments are now in progress in this laboratory.

APPENDIX

First it is to be shown that the distribution law

$$m\{n_s\} = (\sum sN_s)\alpha^{\Sigma n_s - 1}(1-\alpha)^{\Sigma s n_s - 2\Sigma n_s + 2}\frac{(\sum sn_s - \sum n_s)!}{(\sum sn_s - 2\sum n_s + 2)!}\prod_s \frac{w_s^{n_s}}{n_s!} \tag{A1}$$

satisfies the conditions

$$M = \sum_{\text{all }\{n_s\}} m\{n_s\} = (\sum N_s)(1 - \alpha\lambda_n/2), \tag{A2}$$

and

$$N_t = \sum_{\text{all }\{n_s\}} n_t m\{n_s\} \quad \text{(for all } t). \tag{A3}$$

Expanding the power of $(1-\alpha)$ in Eq. (A1), we have

$$M = (\sum sN_s)\sum_{\text{all }\{n_s\}}\sum_k (-1)^k \alpha^{\Sigma n_s + k - 1}\frac{(\sum sn_s - \sum n_s)!}{k!(\sum sn_s - 2\sum n_s + 2 - k)!}\prod_n \frac{w_s^{n_s}}{n_s!}. \tag{A4}$$

By putting $\sum n_s + k = q$ and eliminating k, this may be written

$$M = (\sum sN_s)\sum_{q=1}^\infty \frac{(-\alpha)^q}{q!}\sum_{\Sigma n_s \leq q}\prod_s \frac{(-1)^{\Sigma n_s}q!(\sum sn_s - \sum n_s)!w_s^{n_s}}{n_s!(q - \sum n_s)!(\sum sn_s - \sum n_s + 2 - q)!}, \tag{A5}$$

where the second sum is taken over all sets $\{n_s\}$ satisfying the condition $\sum n_s \leq q$. Consider now the function

$$F(x) = (1 - \sum w_s x^{s-1})^q = \sum_{\Sigma n_s \leq q}\prod_s \frac{(-1)^{\Sigma n_s}q!w_s^{n_s}x^{\Sigma s n_s - \Sigma n_s}}{n_s!(q - \sum n_s)!}, \tag{A6}$$

where q is an integer greater than two. Repeated differentiation gives

$$\left[\left(\frac{d}{dx}\right)^{q-2} F(x)\right]_{x=1} = \sum_{\Sigma n_s \leq q}\prod_s \frac{(-1)^{\Sigma n_s}q!(\sum sn_s - \sum n_s)!w_s^{n_s}}{n_s!(q - \sum n_s)!(\sum sn_s - \sum n_s - q + 2)!}, \tag{A7}$$

which is recognized as a sum required in Eq. (A5). But since this derivative necessarily contains the factor $(1 - \sum w_s)$, its value is zero, and the sum of Eq. (A5) reduces to the terms in $q = 1$ and $q = 2$. Evaluating these, we obtain

$$M = (\sum sN_s)(\sum w_s/s - \alpha/2) = (\sum N_s)(1 - \alpha\lambda_n/2), \tag{A8}$$

where we have used $\sum w_s/s = \sum N_s/\sum sN_s = 1/\lambda_n$. This proves (A2).

We must now evaluate

$$\sum_{\text{all }\{n_s\}} n_t m\{n_s\} = (\sum sN_s)\sum_{\text{all }\{n_s\}}\alpha^{\Sigma n_s - 1}(1-\alpha)^{\Sigma s n_s - 2\Sigma n_s + 2}\frac{(\sum sn_s - \sum n_s)!}{(\sum sn_s - 2\sum n_s + 2)!}\frac{w_t^{n_t}}{(n_t - 1)!}\prod_s{}' w_s^{n_s}/n_s!, \tag{A9}$$

where the prime on the product sign indicates that the term in t is omitted. If we now put $\nu_t = n_t - 1$, and $\nu_s = n_s$, this becomes

$$\sum_{\text{all }\{n_s\}} n_t m\{n_s\} = w_t(\sum sN_s)\sum_{\text{all }\{\nu_s\}}\alpha^{\Sigma \nu_s}(1-\alpha)^{\Sigma s\nu_s - 2\Sigma\nu_s + t}\frac{(\sum s\nu_s - \sum \nu_s + t - 1)!}{(\sum s\nu_s - 2\sum \nu_s + t)!}\prod_s \frac{w_s^{\nu_s}}{\nu_s!}. \tag{A10}$$

As before, we expand the power of $(1-\alpha)$ and obtain

$$\sum_{\text{all }\{n_s\}} n_t m\{n_s\} = w_t(\sum sN_s)\sum_{q=0}^\infty \frac{(-\alpha)^q}{q!}\sum_{\Sigma \nu_s \leq q}\prod_s \frac{(-1)^{\nu_s}(\sum s\nu_s - \sum \nu_s + t - 1)!q!w_s^{\nu_s}}{(\sum s\nu_s - \sum \nu_s + t - q)!(q - \sum \nu_s)!\nu_s!}. \tag{A11}$$

The $(q-1)$st derivative of the function

$$G(x) = x^{t-1}(1-\sum w_s x^{s-1})^q, \quad (q>1),$$ (A12)

vanishes for $x=1$ and shows that only the terms in $q=0$ and $q=1$ of Eq. (A11) contribute to the sum. Evaluating these, we find

$$\sum_{\text{all } \{n_s\}} n_t m\{n_s\} = w_t(\sum s N_s)/t = N_t.$$ (A13)

Thus the assumed distribution law has been shown to satisfy all necessary conditions.

We now turn to a calculation of the weight average molecular size, which from Eqs. (21) and (22) of the text may be written as

$$\bar{P}_w = \sum_{\text{all } \{n_s\}} (\sum s n_s)^2 m\{n_s\}/(\sum s N_s)$$

$$= [\sum_t (t^2 \sum_{\text{all } \{n_s\}} n_t^2 m\{n_s\}) + 2\sum_t \sum_{r>t} (rt \sum_{\text{all } \{n_s\}} n_r n_t m\{n_s\})]/(\sum s N_s).$$ (A14)

The procedure resembles that used above. Putting $\nu_t = n_t - 2$ and $\nu_s = n_s$, we find

$$\sum_{\text{all } \{n_s\}} n_t(n_t-1)m\{n_s\}/(\sum s N_s) = w_t^2 \sum_{\text{all } \{\nu_s\}} \alpha^{\Sigma \nu_s+1}(1-\alpha)^{\Sigma s \nu_s - 2\Sigma \nu_s + 2t - 2} \frac{(\sum s \nu_s - \sum \nu_s + 2t - 2)!}{(\sum s \nu_s - 2\sum \nu_s + 2t - 2)!} \prod_s \frac{w_s^{\nu_s}}{\nu_s!}$$

$$= w_t^2 \alpha \sum_{q=0}^{\infty} \frac{(-\alpha)^q}{q!} \sum_{\Sigma \nu_s \leq q} \prod_s \frac{(-1)^{\Sigma \nu_s}(\sum s \nu_s - \sum \nu_s + 2t - 2)!q! w_s^{\nu_s}}{(\sum s \nu_s - \sum \nu_s + 2t - 2 - q)!(q - \sum \nu_s)! \nu_s!}.$$ (A15)

Now define

$$H(x) = x^{2t-2}(1-\sum w_s x^{s-1})^q.$$ (A16)

Expanding multinomially and differentiating q times, we have

$$\left[\left(\frac{d}{dx}\right)^q H(x)\right]_{x=1} = \sum_{\Sigma \nu_s \leq q} \prod_s \frac{(-1)^{\Sigma \nu_s}(\sum s \nu_s - \sum \nu_s + 2t - 2)!q! w_s^{\nu_s}}{(\sum s \nu_s - \sum \nu_s + 2t - 2 - q)!(q - \sum \nu_s)! \nu_s!}.$$ (A17)

A direct evaluation of this quantity from Eq. (A16) gives

$$\left[\left(\frac{d}{dx}\right)^q H(x)\right]_{x=1} = q![-\sum(s-1)w_s]^q = q!(-1)^q(\lambda_w-1)^q.$$ (A18)

Thus, substituting in Eq. (A15) we find

$$\sum_{\text{all } \{n_s\}} n_t(n_t-1)m\{n_s\}/(\sum s N_s) = w_t^2 \alpha \sum_{q=0}^{\infty} \alpha^q(\lambda_w-1)^q = w_t^2 \alpha/[1-\alpha(\lambda_w-1)].$$ (A19)

Therefore

$$\sum_{\text{all } \{n_s\}} n_t^2 m\{n_s\}/(\sum s N_s) = w_t^2 \alpha/[1-\alpha(\lambda_w-1)] + w_t/t,$$ (A20)

where we have made use of (A13).

The second sum in Eq. (A14) may be found by a similar procedure, the appropriate auxiliary function being $I(x) = x^{r+t-2}(1-\sum w_s x^{s-1})^q$. The result is

$$\sum_{\text{all } \{n_s\}} n_r n_t m\{n_s\}/(\sum s N_s) = w_r w_t \alpha/[1-\alpha(\lambda_w-1)].$$ (A21)

Substituting Eqs. (A20) and (A21) into Eq. (A14), we get

$$\bar{P}_w = [\sum_t t^2 w_t^2 + 2\sum_t \sum_{r>t} rt w_r w_t]\alpha/[1-\alpha(\lambda_w-1)] + \sum_t t w_t = \alpha \lambda_w^2/[1-\alpha(\lambda_w-1)] + \lambda_w$$

$$= \lambda_w(1+\alpha)/[1-\alpha(\lambda_w-1)],$$ (A22)

which is the result given in Eq. (23) of the text.