Elastically Effective Strand Density in Polymer Networks

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ABSTRACT: A new expression is derived which relates the density of elastically effective strands in a polymer network to the densities of random cross-links, main-chain scissions, and entanglements and to the molecular weight distribution of the initial linear polymer. Methods are recommended for characterizing the cross-link and scission densities from measurable sol fractions and for determining the entanglement density empirically. The strand density can be evaluated quite easily for the random and uniform initial molecular weight distributions. The new expression differs appreciably from that of Mullins and Bueche, owing principally to a new criterion for effectively trapping network entanglements. The statistical approach used to derive the strand density is also used in a new derivation of an existing implicit expression for the gel fraction.

Both the equilibrium elastic compliance[1] and the equilibrium degree of swelling[2] of cross-linked elastomeric polymers have been theoretically related to the number of elastically effective network strands per unit volume, ν. Furthermore, recent work[3] on such systems suggests that the increase of the viscoelastic storage compliance, as it approaches its equilibrium value with decreasing frequency, is related to a decrease in the elastically effective strand density due to relaxation of certain network entanglements. In applying these quantitative relations, it is very useful to relate the strand density ν to the network structure. To do this Mullins[4] and Bueche[5] have proposed equivalent expressions for ν. In Bueche's notation

$$\nu = 2C - 2\rho/\bar{M}_n + 2\epsilon(1 - \rho/C\bar{M}_n) \qquad (1)$$

where C is the density of chemical cross-links, ρ is the polymer mass density, $\bar{M}_n$ is the number-average molecular weight before cross-linking, and 2ϵ is the maximum potential contribution of entanglements to ν. In this equation, the three terms on the right side represent, respectively, the direct contribution of chemical cross-links, the correction due to original chain ends, and the contribution of entanglements trapped between cross-links.[5]

To include lightly cross-linked networks, eq 1 should be generalized by excluding from consideration the appreciable fraction of polymer (sol fraction) not bonded to the continuous gel network, and thus unable to contribute to ν. If main-chain scission occurs during cross-linking, eq 1 should be further generalized to include the effect on ν. Finally, a more rigorous term should be used to express the trapped entanglement contribution to ν. In this paper, these considerations are applied to relate ν to the network structure by a new expression. The network structure, in turn, is characterized here by measurable sol fractions. The application of the new relations is illustrated in the following paper.[3]

Characterization of Network Structure

Lightly cross-linked elastomers have an appreciable sol weight fraction w_s and, with good solvents, the networks can be highly swollen to extract the sol fraction quantitatively. To characterize the network structure, this measurable sol fraction can be related to the densities of cross-links and main-chain scissions for certain cross-linking conditions by derivations such as the following.

The cross-linking conditions of interest are those commonly assumed in prior treatments of network formation statistics.[6-8] An initially linear polymer is assumed to have undergone random cross-linking and main-chain scission. It is assumed that the fraction of possible points which have actually experienced cross-linking or scission is much less than unity and that no end-linking by scission products has occurred. We disregard intramolecular cross-links between two points caused by the previous connecting structure.

Let p and q be the probabilities that a randomly chosen monomer unit in the system has experienced scission or shares a cross-link, respectively. In the initial system, consider the nth monomer unit from one end of a molecule. After cross-linking and scission, the probability that a route from this unit toward the specified end leads to the gel fraction is the probability that a cross-link to the final gel fraction is encountered before reaching either a scission point or the specified end. If w_g is the gel weight fraction ($= 1 - w_s$), this probability $g(n)$ is given by

$$g(n) = \sum_{i=1}^{n} qw_g(1 - qw_g)^i(1 - p)^i \qquad (2)$$

where the probability of first encountering a cross-link to the gel without prior scission is summed over all of the n units at which this can occur. Letting $x = qw_g/(p + qw_g)$ and $y = p + qw_g$ and recalling the assumption that p and $q \ll 1$, we obtain

$$g(n) = xy \sum_{i=1}^{n} (1 - y)^i$$

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(1) P. J. Flory, *Chem. Rev.*, **35**, 51 (1944).

(2) P. J. Flory and J. Rehner, Jr., *J. Chem. Phys.*, **11**, 521 (1943); P. J. Flory, *ibid.*, **18**, 108 (1950).

(3) N. R. Langley and J. D. Ferry, *Macromolecules*, **1**, 353 (1968).

(4) C. G. Moore and W. F. Watson, *J. Polym. Sci.*, **19**, 237 (1956).

(5) A. M. Bueche, *ibid.*, **19**, 297 (1956).

(6) W. H. Stockmayer, *J. Chem. Phys.*, **12**, 125 (1944).

(7) P. J. Flory, *J. Amer. Chem. Soc.*, **69**, 30 (1947).

(8) A. Charlesby, *Proc. Roy. Soc.* (London), **A222**, 542 (1954).

or

$$g(n) = x(1 - e^{-yn}) \qquad (3)$$

We now evaluate the probability $g(n,P)$ that the nth monomer unit from one end of a molecule of P units in the initial system becomes connected to the gel fraction by *any* route. It is the probability of connecting to the gel by a route toward one end plus, if this fails, the probability by a route toward the other end. Thus

$$\begin{aligned} g(n,P) &= g(n) + [1 - g(n)]g(P - n) \\ &= g(n) + g(P - n) - g(n)g(P - n) \end{aligned}$$

or, by eq 3

$$\begin{aligned} g(n,P) = x[2 - e^{-yn} - e^{-y(P-n)}] - \\ x^2[1 - e^{-yn} - e^{-y(P-n)} + e^{-yP}] \quad (4) \end{aligned}$$

For a general initial molecular weight distribution, where N_P is the mole fraction of molecules with degree of polymerization P, the gel fraction is obtained by averaging $g(n,P)$ over all monomer units in the system. Thus

$$w_g = \sum_{P=1}^{\infty} \sum_{n=1}^{P} g(n,P)N_P / \sum_{P=1}^{\infty} PN_P \qquad (5)$$

where the denominator is $\bar{P}_n$, the number-average degree of polymerization. Substituting $g(n,P)$ from eq 4, we obtain the desired result

$$\begin{aligned} w_g = 2x[1 - (1 - \sum_{P=1}^{\infty} N_Pe^{-yP})/y\bar{P}_n] - \\ x^2[1 - 2(1 - \sum_{P=1}^{\infty} N_Pe^{-yP})/y\bar{P}_n + \\ (1/\bar{P}_n) \sum_{P=1}^{\infty} PN_Pe^{-yP}] \quad (6) \end{aligned}$$

By replacing the e^{-yP} factors with their series expansion, eq 6 may be expressed alternatively in terms of the various degree-of-polymerization averages defined as

$$\begin{aligned} \bar{P}_w = (1/\bar{P}_n)(\sum_{P=1}^{\infty} P^2N_P), \bar{P}_z = (1/\bar{P}_n\bar{P}_u) \sum_{P=1}^{\infty} P^3N_P, \\ \bar{P}_{z+1} = (1/\bar{P}_n\bar{P}_w\bar{P}_z) \sum_{P=1}^{\infty} P^4N_P, \text{ etc.} \end{aligned}$$

Thus

$$\begin{aligned} w_g = 2x[y\bar{P}_w/2! - y^2\bar{P}_u\bar{P}_z/3! + \\ y^3\bar{P}_u\bar{P}_z\bar{P}_{z+1}/4! - \ldots] - x^2[(1/3!)y^2\bar{P}_w\bar{P}_z - \\ (2/4!)y^3\bar{P}_u\bar{P}_z\bar{P}_{z-1} + (3/5!)y^4\bar{P}_w\bar{P}_z\bar{P}_{z+1}\bar{P}_{z+2} - \ldots] \quad (7) \end{aligned}$$

For the special case of no scission, eq 6 and 7 reduce to forms given by Flory[7] and Charlesby,[8] respectively.

Inokuti,[9] by considering the changing molecular weight distribution during first scission then cross-linking steps, has also obtained an implicit expression for the gel fraction for a general initial molecular weight distribution. His eq 10, resulting from this entirely different approach, can be shown to be equivalent to eq 6 above. The somewhat more direct derivation presented in this paper produces the intermediate expression for $g(n)$ which is required in the following section. This derivation also contributes an approach for determining other structural properties of randomly formed networks such as the distribution of lengths of strands between cross-links or the number of various branched free end structures which may control the rate of relaxation of entanglements.[3]

Equation 6 or 7 from the preceding derivation relates the densities of cross-linking and scission to the gel fraction and initial molecular weight distribution. To determine simultaneously both of these unknown densities, the relation must be applied to at least two systems, (1) and (2), in which the ratios p_2/p_1 and q_2/q_1 are known. If the networks are formed by ionizing radiation, for example, both ratios might be assumed to equal the ratio of radiation exposures.

A trial and error scheme for calculating p_1 and q_1 from the initial molecular weight distribution, the measured gel fractions of two systems, $w_{g,1}$ and $w_{g,2}$, and the exposure ratio p_2/p_1 ($= q_2/q_1$) is the following. (a) From a trial value of y_1 and the initial molecular weight distribution, evaluate the two bracketed quantities (denoted a and b, respectively) in eq 6 or 7. (b) Calculate x_1 from the solution (eq 8) of these quadratic equations. (c) Calculate y_2 and x_2 from the ratio

$$x_1 = [a_1 - (a_1^2 - b_1w_{g,1})^{1/2}]/b_1 \qquad (8)$$

p_2/p_1 by eq 9 and 10 arising from the definitions of x and y. (d) Calculate $w_{g,2}$ from y_2, x_2, and the molecular weight distribution by eq 6 or 7. (e) Repeat steps a–d with additional trial values of y_1 until the calculated $w_{g,2}$ value from step d agrees with the measured value. The values of p_1 and q_1 are then calculated from x_1 and y_1 values in the final trial calculation as

$$y_2 = y_1(p_2/p_1)[1 + x_1(w_{g,2}/w_{g,1} - 1)] \qquad (9)$$

$$x_2 = x_1y_1p_2w_{g,2}/y_2p_1w_{g,1} \qquad (10)$$

$$p_1 = y_1(1 - x_1) \qquad (11)$$

and

$$q_1 = x_1y_1/w_{g,1} \qquad (12)$$

If the initial molecular weight distribution is of the "generalized Poisson" type, numerical results of Inokuti[9] allow more rapid calculation of p_1 and q_1 than do steps a–e above. For the "random" initial distribution, eq 6 reduces to the result of Charlesby and Pinner,[10] eq 29 below, and their method of plotting $(w_s + w_s^{1/2})$ against the reciprocal of the radiation exposure yields p and q directly. Other special initial distributions or the absence of scission will also simplify eq 6 and 7 to facilitate characterization of the network structure from w_g data.[3,7,8]

If the ratio of the scission and cross-linking rates p/q is known independently, the gel fraction of only one system is sufficient to determine p and q. Only step a is then required since x calculated from its definition in the form

$$x = w_g/(p/q + w_g) \qquad (13)$$

may be used with a and b values from step a to calculate

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(9) M. Inokuti, *J. Chem. Phys.*, **38**, 2999 (1963).

(10) A. Charlesby and S. H. Pinner, *Proc. Roy. Soc.* (London), **A249**, 367 (1959).

w_g from eq 6 or 7 for comparison with the measured value of w_g. Again, Inokuti's tables[9] may be used to determine p and q more rapidly for the generalized Poisson initial molecular weight distribution.

Relation of Elastically Effective Strand Density to Network Structure

Once the cross-linking and scission densities of the network have been characterized, ν may be determined. To do this, the first two terms on the right side of eq 1 must be generalized by recognizing that only strands in the gel fraction can be elastically effective at mechanical equilibrium. The density of chemical cross-links in the gel fraction is greater than in the system as a whole by the factor $(1 + w_s)$ or $(2 - w_g)$, as shown by Flory.[7] Thus, the term $2C$ (or $q\rho/M_0$ where M_0 is the monomer molecular weight), the total moles of cross-linked units per cubic centimeter of the whole system, must be replaced by

$$q\rho(2 - w_g)w_g/M_0 \qquad (14)$$

the moles of cross-linked units in the *gel fraction* per cubic centimeter of the *whole system.*

To generalize the second term of eq 1, we require the moles of original chain ends in the gel fraction per cubic centimeter of the whole system. If the initial molecular weight distribution is not uniform or if scission occurs, thereby broadening the initially uniform distribution, the longer molecules present are more likely to be cross-linked to the gel fraction than are the shorter ones. Thus, in the gel fraction, the density of original ends will be less than in the system as a whole. The probability that an original end of a molecule of initial degree of polymerization P is in the gel fraction is simply $g(P)$. Therefore, of the $2\rho/\bar{M}_n$ total moles of original ends per cubic centimeter of the whole system, the number in the gel fraction is

$$(2\rho/\bar{M}_n) \sum_{P=1}^{\infty} g(P)N_P$$

Evaluating $g(P)$ from eq 3, we obtain the desired second term as

$$(2\rho x/\bar{M}_n)(1 - \sum_{P=1}^{\infty} N_P e^{-yP}) \qquad (15)$$

An additional term, the moles of *scission-produced* chain ends in the gel fraction per cubic centimeter of the whole system, must also be subtracted in generalizing eq 1. These scission ends are entirely equivalent to original chain ends in their effect[1] on ν. The probability that a random scission end leads to the gel fraction in the one possible direction is simply $g(n)$ averaged over all monomer units in the system. Therefore, of the $2p/M_0$ total moles of scission ends per cubic centimeter of the whole system, the number in the gel fraction is

$$(2p\rho/M_0)(1/\bar{P}_n) \sum_{P=1}^{\infty} \sum_{n=1}^{P} g(n)N_P$$

Substituting $g(n)$ from eq 3 yields the desired additional term as

$$(2\rho px/M_0)[1 - (1 - \sum_{P=1}^{\infty} N_P e^{-yP})/y\bar{P}_n] \qquad (16)$$

The third term on the right side of eq 1 is 2ϵ, the maximum potential contribution of entanglements to ν, multiplied by a factor, $(1 - \rho/C\bar{M}_n)$, which is used to represent the fraction of the system that exists as strands between cross-links. This factor is assumed to equal the fraction of potential entanglements that are trapped between cross-links, thus effective at mechanical equilibrium. It is considered here that a more appropriate factor for the fraction of entanglements trapped, T_e, is the probability that all of the four directions from two randomly chosen points in the system, which may potentially contribute an entanglement, lead to the gel fraction. If one or more of the four directions lead to structures of finite size rather than to the gel, then the potential entanglement is not considered trapped.[11,12]

The probability that both directions from one randomly chosen point lead to the gel fraction is $g(n)g \cdot (P - n)$ averaged over all monomer units in the system. Therefore

$$T_e = [(1/\bar{P}_n) \sum_{P=1}^{\infty} \sum_{n=1}^{P} g(n)g(P - n)N_P]^2$$

The second term on the right side of eq 4 is $g(n)g(P - n)$. Substitution of this term in the above equation gives $T_e^{1/2}$ as the second term on the right side of eq 6 or 7. Thus

$$T_e = x^4[1 - 2(1 - \sum_{P=1}^{\infty} N_P e^{-yP})/y\bar{P}_n + (1/\bar{P}_n) \sum_{P=1}^{\infty} PN_P e^{-yP}]^2 \qquad (17)$$

or

$$T_e = x^4[(1/3!)y^2\bar{P}_w\bar{P}_z - (2/4!)y^3\bar{P}_w\bar{P}_z\bar{P}_{z+1} + (3/5!)y^4\bar{P}_w\bar{P}_z\bar{P}_{z+1}\bar{P}_{z+2} - \ldots]^2 \qquad (18)$$

Expressions 14–17 are now used as indicated above to replace eq 1, giving the desired general relation between ν and the network structure. Using the definitions of x and y and eq 6 and 17, the new terms combine quite remarkably to give

$$\nu = (q\rho/M_0)w_g T_e^{1/2} + 2\epsilon T_e \qquad (19)$$

Both w_g and T_e are given in terms of p, q, and N_P by eq 6 and 17 and the definitions of x and y; thus eq 19 relates ν to the independent structural variables p, q, N_P, and ϵ.

Since even trapped entanglements may be less effective than chemical cross-links as network constraints, ϵ in eq 19 should be regarded as the product of the potential entanglement density and the effectiveness of a trapped entanglement relative to a chemical cross-link. The value of ϵ is assumed to be independent of p, q, and N_P for a given polymer and can be empirically determined. One method of determining ϵ for a polymer from values of q, w_g, and T_e for several charac-

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(11) Trapping does not require, however, two "closed, interpenetrating loops" of a particular size, as in a treatment by Case and Wargin,[12] since a constraint clearly exists if the four directions merely lead to the gel.

(12) L. C. Case and R. V. Wargin, *Makromol. Chem.*, 77, 172 (1964).

terized networks is to plot $(g\nu)/T_e$ against $(q\rho/M_0)\cdot w_g T_e^{-1/2}$. The product $g\nu$ could be determined from the measured equilibrium shear compliance J_e by the relation

$$g\nu = 1/J_e RT \tag{20}$$

from the theory of rubberlike elasticity[13] where g is considered an unknown constant, R is the gas law constant, and T is the absolute temperature. From eq 19

$$g\nu/T_e = g(q\rho/M_0)w_g T_e^{-1/2} + 2g\epsilon \tag{21}$$

which predicts a linear plot with slope of g and intercept-to-slope ratio of 2ϵ.[14]

For the special case of no scission and a uniform initial molecular weight M, ν may be expressed directly in terms of w_g. Equation 6 for this case reduces to Flory's result[7]

$$w_g = 1 - e^{-qPw_g}$$

or

$$qP = -[\ln(1 - w_g)]/w_g \tag{22}$$

By applying this relation, eq 17 reduces to

$$T_e = [2 - w_g + 2w_g/\ln(1 - w_g)]^2 \tag{23}$$

Substitution of eq 22 and 23 into eq 19 gives

$$\nu = (\rho/M)[(w_g - 2)\ln(1 - w_g) - 2w_g] + 2\epsilon[2 - w_g + 2w_g/\ln(1 - w_g)]^2 \tag{24}$$

A less restricted special case in which the expressions for w_g, T_e, and ν simplify is that of the initial distribution

$$N_P = (1/\bar{P}_n)e^{-P/\bar{P}_n} \tag{25}$$

This has been called the "random," "exponential," and "most-probable" distribution and is identical[10] with that produced by $1/\bar{P}_n$ random scissions per monomer unit in a hypothetical system of infinite initial molecular weight ($N_P = 0$ for finite P). Equation 6 for this infinite initial molecular weight distribution reduces to

$$w_g = 2x' - (x')^2 \tag{26}$$

where

$$x' = qw_g/(p + 1/\bar{P}_n + qw_g) \tag{27}$$

to include the $(p + 1/\bar{P}_n)$ total scission probability. The solution of eq 26 is

$$x' = 1 - w_s^{1/2} \tag{28}$$

and substitution of eq 27 for x' yields the result of Charlesby and Pinner.[10]

$$w_s + w_s^{1/2} = 1/q\bar{P}_n + p/q \tag{29}$$

Equation 17 similarly reduces to $T_e = (x')^4$, yielding, from eq 28, the simple result

$$T_e = (1 - w_s^{1/2})^4 \tag{30}$$

or, from eq 29

$$T_e = \{3 - [1 + 4(1 + p\bar{P}_n)/q\bar{P}_n]^{1/2}\}^4/16 \tag{31}$$

Thus, eq 19 becomes, in terms of q and w_s

$$\nu = (q\rho/M_0)(1 - w_s)(1 - w_s^{1/2})^2 + 2\epsilon(1 - w_s^{1/2})^4 \tag{32}$$

for the random initial molecular weight distribution including scission as well as cross-linking. Again, since w_s is given in terms of the basic structural variables by eq 29, eq 32 relates ν to these variables.[15–18]

Comparison of Result with Previous Expression for ν

In comparing eq 19 with the Mullins–Bueche expression (eq 1), the terms representing the cross-link and chain-end contributions are considered first. These terms in eq 1, $2C - 2\rho/\bar{M}_n$, may be expressed in the notation of this paper as

$$(q\rho/M_0)(1 - 2/q\bar{P}_n)$$

for comparison with the corresponding term from eq 19

$$(q\rho/M_0)w_g T_e^{1/2}$$

For the uniform initial molecular weight distribution with no scission, values of the term from eq 1 are smaller than those from eq 19 by less than 2% for values of $q\bar{P}_n \equiv \gamma$, the cross-linking index, greater than four cross-linked units per initial molecule. For the random initial distribution with no scission, this is true for

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(13) J. D. Ferry, "Proceedings of the International Conference on Physics of Non-Crystalline Solids," North-Holland Publishing Co., Amsterdam, 1965, p 333.

(14) With increasing cross-linking, the ordinate and abscissa values decrease linearly, then increase to retrace the linear plot. The $g\nu$ data must be quite precise to obtain good linearity since the available range of $g\nu/T_e$ values may be a small fraction of the magnitude.

(15) Scanlan[16] has also shown that Flory's analysis[1] of the effect of chain ends, as applied to the gel fraction, yields the first terms on the right sides of eq 24 and 32 as ν for the above two special cases (Scanlan's eq 29 and 16, respectively, where $s_1^2 = w_s$). Scanlan does not consider entanglements nor give any expression for a general initial molecular weight distribution such as eq 19. His own network analysis, giving the effective strand density as two times the density of cross-links which lead to gel in four directions plus 1.5 times the density of those leading to gel in three directions, his eq 10, is believed to be less rigorous than Flory's[1] analysis. For example, a new cross-link joining two of Scanlan's "trifunctional junctions" at points on the free end strands produces two "tetrafunctional junctions" instead, increasing, by Scanlan's eq 10, the effective strands by $2(2 - 3/2) = 1$. If, however, the new cross-link joins the two trifunctional junctions at points on strands leading toward the gel, a difference of no actual consequence since the points may be taken arbitrarily close to the junctions, the two trifunctional junctions remain while the new cross-link itself adds one tetrafunctional junction, increasing, by Scanlan's eq 10, the effective strands by two. Thus, Scanlan's analysis is inconsistent in this example while Flory's analysis[1] consistently predicts two new effective strands in either case. Other network analyses,[17,18] which use bases similar to Scanlan's[16] for counting effective strands, are thus considered less rigorous than the present application of Flory's analysis.

(16) J. Scanlan, *J. Polym. Sci.*, **43**, 501 (1960).

(17) L. Mullins and A. G. Thomas, *ibid.*, **43**, 13 (1960).

(18) G. R. Dobson and M. Gordon, *J. Chem. Phys.*, **43**, 705 (1965).

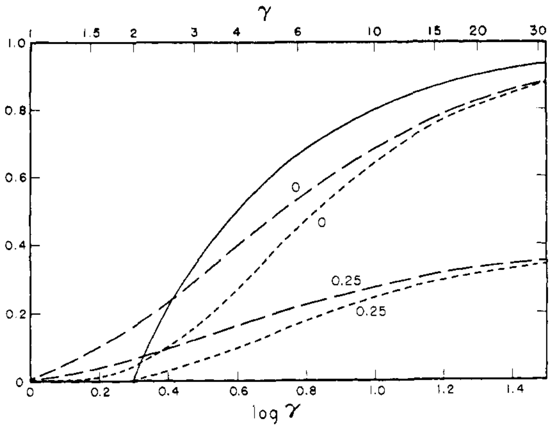

Figure 1. Calculated fraction of entanglements trapped, T_e, *vs.* cross-linking index (cross-linked units per number-average initial molecule), $\gamma \equiv q\bar{P}_n$. Solid curve from Mullins–Bueche relation; other curves from present treatment with long dashes for random initial molecular weight distribution and short dashes for uniform distribution. Values for ratio of scissions to cross-linked units, p/q, are indicated.

$q\bar{P}_n > 11$. Of course, if scission occurs with either distribution, the deviations may be of much greater magnitude since scission is not considered in eq 1.

In the absence of scission, these deviations in the cross-link and chain-end terms are thus negligible for all except quite lightly cross-linked systems. The deviations for the lightly cross-linked systems are usually unimportant since it is the entanglement term in eq 19 which is the major contribution to ν for such systems. This is true since $q\rho/M_0$ in eq 19, the density of cross-linked units, is usually several times less than 2ϵ for such systems while w_g is of the same order of magnitude as $T_e^{1/2}$, somewhat less than unity. Therefore, it is the entanglement terms in eq 1 and 19 that now must be compared to determine any significant over-all deviations in these expressions for ν.

The entanglement terms are compared by evaluating the entanglement trapping factors in eq 1 and 19 and plotting in Figure 1. For eq 1 we have

$$T_e = 1 - \rho/C\bar{M}_n = 1 - 2/q\bar{P}_n \qquad (33)$$

For eq 19, T_e is evaluated for the random initial molecular weight distribution with p/q values of 0 and 0.25 by eq 31. Equations 22 and 23 are used to evaluate T_e for the uniform initial distribution with $p/q = 0$ while eq 6 and 7 give T_e with $p/q = 0.25$ for this distribution.

Figure 1 shows that the function T_e derived in this paper with $p/q = 0$ for both of the initial distributions is appreciably different from the trapping factor used by Mullins and Bueche. The occurrence of a moderate amount of scission is also seen to reduce sharply the limiting value of T_e at high degrees of cross-linking, $T_{e,\max}$. From eq 31 this limit is

$$T_{e,\max} = [3 - (1 + 4p/q)^{1/2}]^4/16 \qquad (34)$$

for $p/q \leq 2$. The effect of the initial molecular weight distribution on T_e is significant for lower degrees of cross-linking. It is apparent that eq 19 predicts an appreciably different dependence of ν on the structural variables.

The new relation not only generalizes the Mullins–Bueche relation to include lightly cross-linked systems and systems which have experienced scission, but also predicts entanglement contributions that are appreciably different up to rather high degrees of cross-linking.

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