

CHROM. 4972

CHARACTERISATION OF POLYDISPERSE BRANCHED POLYMERS
BY MEANS OF GEL PERMEATION CHROMATOGRAPHY

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SUMMARY

Theoretical gel permeation chromatography curves have been derived for model polydisperse polymers having chosen molecular weight averages and a given degree of random trifunctional branching. Gel permeation chromatography traces had been treated on a computer using the method proposed by DROTT, and the molecular weight averages and a branching characteristic obtained were compared with those following directly from the model used (the STOCKMAYER type of distribution). The basic assumption of DROTT (the ratio of the number of branch points to the molecular weight being constant) is discussed.

INTRODUCTION

Gel permeation chromatography provides an extremely convenient and rapid method for determination of the molecular weight distribution of polydisperse linear polymers. With polydisperse branched polymers, on the other hand, interpretation of the gel permeation chromatography (GPC) traces in terms of molecular weight averages and branching densities is considerably complicated by a distribution, not only of molecular weights, but of branch points. Two attempts¹⁻⁴ have been made to analyse gel permeation chromatograms of polydisperse branched polymers. Both methods assume, *a priori*, a branching distribution. Thus DROTT *et al.*¹⁻³ assume that the number of branch points, n_M , per molecule is proportional to the molecular weight, M , while SHULTZ⁴ assigns a definite distribution of both branch points and molecular weights to the branched polymer.

The branching model assumed by DROTT is likely to be in error, particularly at low molecular weights, for most real polymers. It is, however, difficult to predict how seriously this assumption affects the calculated molecular parameters. The validity of DROTT's method has been checked by calculating theoretical gel permeation chromatograms for a polydisperse branched polymer conforming to a distribution of n and M first derived by STOCKMAYER⁵ and for which n_M is not proportional to M over the whole molecular weight range. The theoretical GPC traces were analysed according to the method of DROTT and the molecular parameters obtained compared with those used to calculate the GPC trace.

THEORETICAL GEL PERMEATION CHROMATOGRAMS

A gel permeation chromatogram is, in effect, a plot of the weight fraction W_v of polymer having an elution volume V against V . On the other hand, the molecular weight distribution of a polydisperse branched polymer is usually^{4,6-8} more conveniently expressed in terms of the differential weight fraction W_z of polymer having a relative molecular weight Z and having an average number n_z of branch points. Here Z is a reduced variable defined as $Z = M/\bar{Y}_n$, where \bar{Y}_n is the number average molecular weight of the "primary" chains, *i.e.* the number average molecular weight which would be obtained if all the branches were severed. In order therefore to construct a theoretical GPC trace for a polydisperse branched polymer, W_v must be written in terms of W_z , and the elution volume V corresponding to each Z -mer calculated.

The latter calculation requires knowledge of the "universal" calibration curve for the particular GPC column set under its operating condition, *i.e.* the constants A, B, C , etc. in the equation

$$\log [\eta]M = A + BV + CV^2 + \dots \quad (1)$$

must be known. ($[\eta]$ is the intrinsic viscosity.) As shown by SHULTZ⁴, the elution volume for each Z -mer is given by

$$\log ([\eta]Z) = A' + B'V + C'V^2 + \dots = \log K' + (\frac{1}{2}) \log g_z + (1 + a) \log Z \quad (2)$$

The constants a and K' occur in the intrinsic viscosity-molecular weight relationship for the monodisperse linear polymer in the GPC solvent at its operating temperature, *i.e.*

$$[\eta]_L = KM^a = K'Z^a \quad (3)$$

The branching parameter g_z in eqn. 2 is a function of n_z , being related to the intrinsic viscosities of the branched and linear chains of the same molecular weight by⁹

$$g_z^{1/2} = f(n_z) \simeq [\eta]_B/[\eta]_L \quad (4)$$

Expressions relating g_z to n_z have been calculated¹⁰⁻¹² for various branching topologies. If the dependence of n_z on Z is known, the relationship between g_z and Z can be calculated; hence V can be obtained for each Z -mer from eqn. 2.

It follows from eqn. 1 that W_v corresponds to the weight fraction $W_{\log[\eta]Z}$ of polymer having logarithm of the product intrinsic viscosity and molecular weight $\log [\eta]Z$. It is readily shown that

$$W_v = W_{\log[\eta]Z} [d \log [\eta]Z / dV] \quad (5)$$

Combining this equation with the relationship between $W_{\log[\eta]Z}$ and W_z derived by SHULTZ for a branched polymer (eqn. 7 of ref. 4) yields the desired dependence of W_v on W_z , namely

$$W_v = g_z^{1/2} Z^{1+a} \left[\frac{d(g_z^{1/2} Z^{1+a})}{dZ} \right]^{-1} \left[\frac{d \log ([\eta]Z)}{dV} \right] W_z \quad (6)$$

Construction of a theoretical gel permeation chromatogram from eqns. 2 and 6 requires knowledge of the functions W_z and g_z . A model polydisperse polymer with trifunctional branch points distributed randomly was used for this purpose. The differential weight fraction distribution functions for such a polymer were first derived by STOCKMAYER⁵; they apply to polymers formed by polycondensation of monomers of the type $XA_2 + YA_3 + ZB_2$ (where A reacts only with B and *vice versa*, and all reacting groups have the same reactivity). We use the slightly modified distribution function of SHULTZ^{4,8}:

$$W_{nz} = [\gamma Z^2/n(n+2)]W_{n-1,z}, \quad n \geq 1 \quad (7)$$

$$W_{0z} = Z e^{-Z(\gamma+1)}$$

and

$$W_z = \sum_{n=0}^{\infty} W_{nz}$$

Here γ is a branching index, being zero for a linear chain and unity at the point of incipient gelation; γ is related to the weight average number \bar{n}_w of branch points per molecule and to the polydispersity factor $\bar{M}_w/\bar{M}_n = Q$ by^{4,5}

$$\gamma = \bar{n}_w/(2 + \bar{n}_w) = 3(Q-2)/(3Q-2) \quad (8)$$

For this model polymer, ZIMM AND STOCKMAYER¹⁰ calculated g_z as a function of n_z :

$$g_z \simeq \{[1 + (n_z/7)]^{1/2} + 4n_z/9\pi\}^{-1/2} \quad (9)$$

where

$$n_z = \frac{\sum_{n=0}^{\infty} nW_{nz}}{\sum_{n=0}^{\infty} W_{nz}}$$

SHULTZ⁸ has tabulated W_z and n_z for various values of Z and for different values of γ . Using these tabulated results and the simplified expressions⁸ for g_z and W_z at large (>120) Z allows the gel permeation chromatography trace to be constructed from eqns. 1, 2, 6 and 9. An actual (non-linear) universal calibration curve was used for this purpose (Fig. 1). This curve was obtained with column combinations of 3×10^5 , 3×10^4 , 3×10^3 and 60 Å using polystyrene fractions in 1,2,4-trichlorobenzene at 135° with a flow rate of 1 ml/sec. The constants K and a in eqn. 2 were given values of 9.54×10^{-4} dl/g and 0.64, respectively; these values were obtained in this laboratory for fractions of linear polyethylene in trichlorobenzene at 135°.

Fig. 2 shows theoretically calculated curves of W_v versus V for polymers having a constant weight-average molecular weight \bar{M}_w of 2×10^5 but with different values of the branching index γ (0, 0.6 and 0.9). Obviously the molecular weight distribution width increases with increasing degree of branching. Of more interest is Fig. 3, which shows the effect on the shape of the gel permeation chromatography trace of changing molecular weight at constant degree of branching ($\gamma = 0.9$, $\bar{n}_w = 18$) and hence constant polydispersity Q . Despite the fact that the distribution of M and n is identical

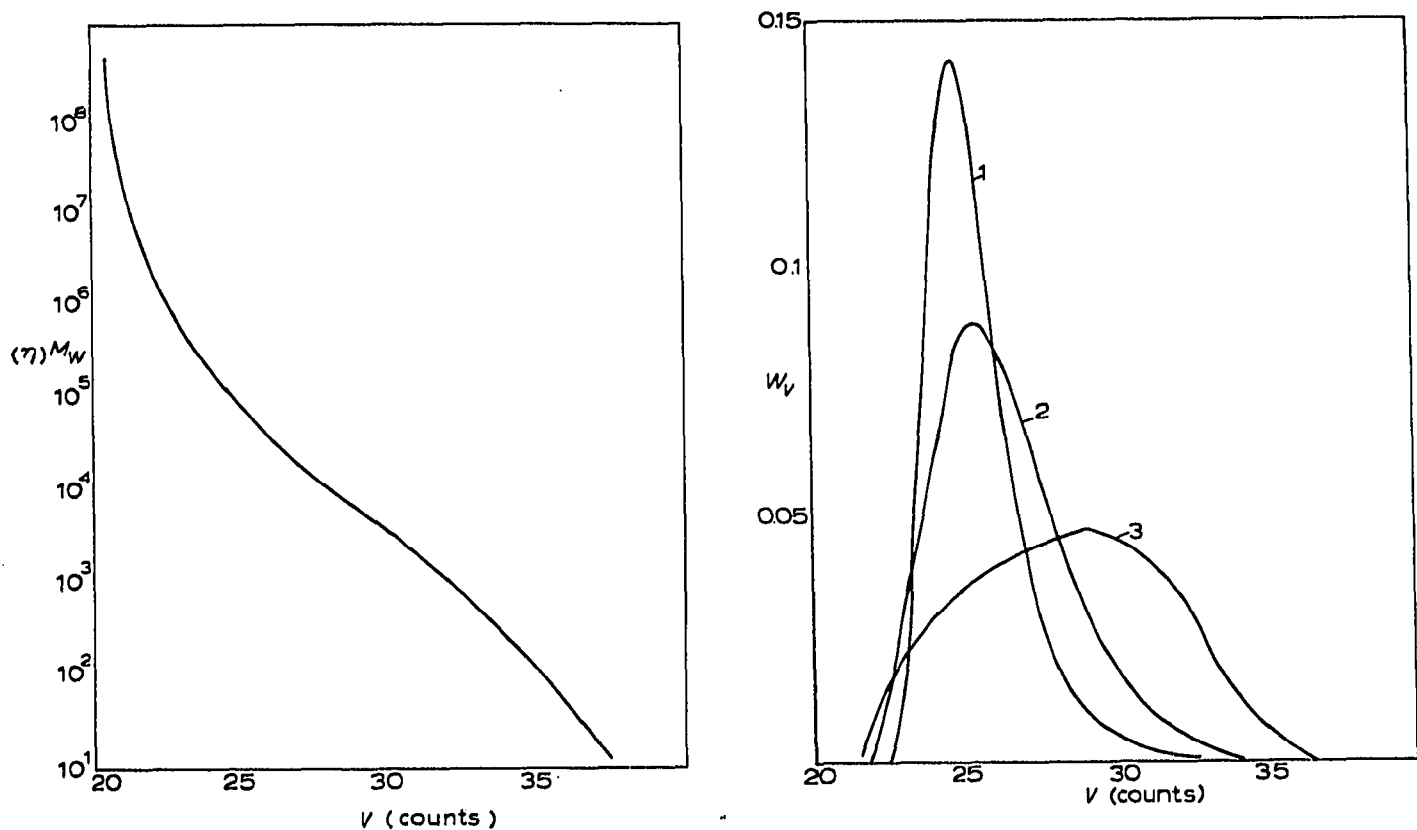


Fig. 1. The universal calibration established experimentally and used throughout all calculations.

Fig. 2. GPC curves for polydisperse branched polymers with $\bar{M}_w = 2 \times 10^6$ and different degrees of branching. (1) $\gamma = 0.0$; (2) $\gamma = 0.6$; (3) $\gamma = 0.9$.

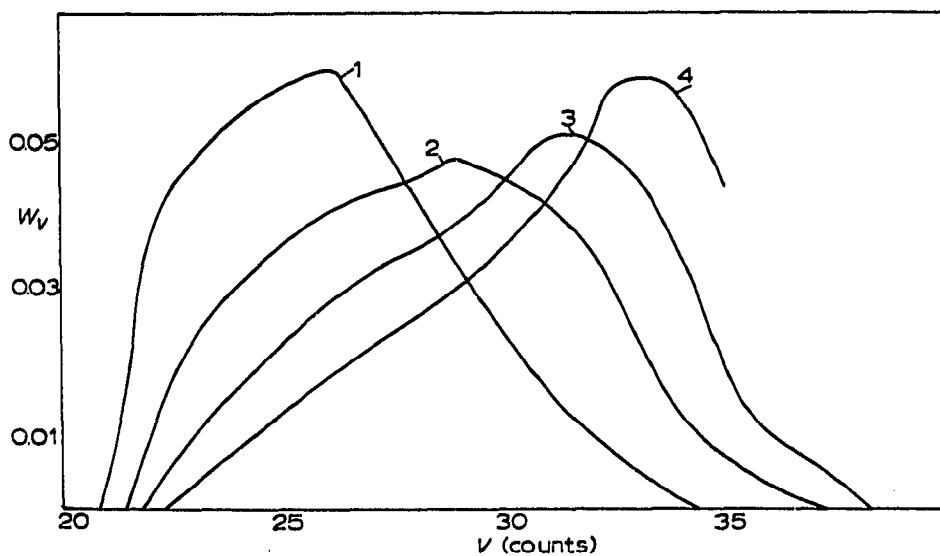


Fig. 3. GPC curves for polydisperse branched polymers with the degree of branching $\gamma = 0.9$ and different molecular weights. (1) $\bar{M}_w = 6 \times 10^6$; (2) $\bar{M}_w = 2 \times 10^6$; (3) $\bar{M}_w = 1.0 \times 10^6$; (4) $\bar{M}_w = 0.5 \times 10^6$.

for each of these curves, there are significant differences in the shapes of the GPC traces for the different \bar{M}_w . In particular, the appearance of shoulders at varying elution volumes is noteworthy. The actual differential distribution curves of W_z versus Z (Fig. 4) do not show such shoulders. In the GPC traces, the latter arise from the use of a non-linear universal calibration curve. For such a curve, the slope $d \log([\eta]Z)/dV$ appearing in eqn. 6 is not a constant; this fact alone accounts for the appearance of shoulders and the different shapes of the curves in Fig. 3. Similar effects were found by YAU *et al.*¹³. This result has an important practical consequence: qualitative conclusions about the molecular weight distribution (such as association of shoulders with an excess of a certain molecular weight species) drawn from visual observation of a gel permeation chromatography trace can be misleading, particularly when a broad molecular weight distribution polymer (branched or linear) is combined with a non-linear calibration curve.

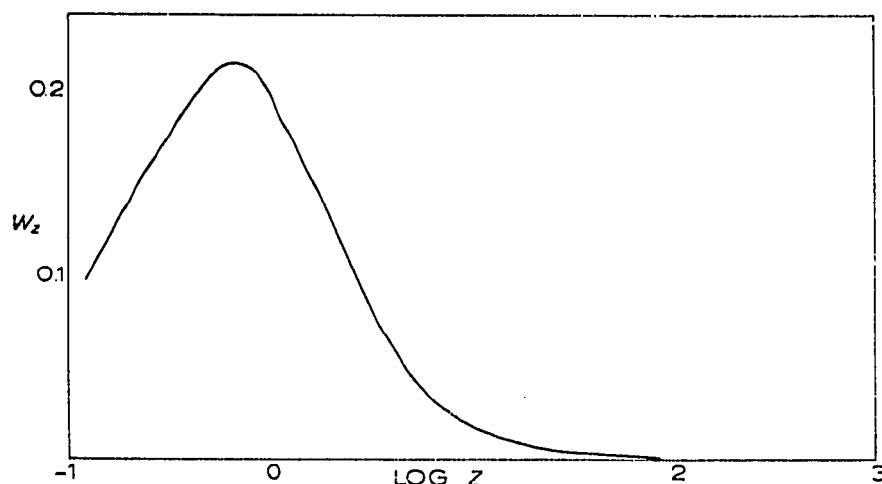


Fig. 4. Differential molecular weight distribution function of STOCKMAYER'S type of branched polymers ($\gamma = 0.9$, Z is the reduced molecular weight).

The validity of the calculated gel permeation chromatograms was checked by assuming the polymers were linear and analysing the gel permeation chromatography trace in the usual manner for a linear polymer. The molecular weights $(\bar{M}_n)_{app}$, $(\bar{M}_w)_{app}$ and $(\bar{M}_z)_{app}$ so obtained are of course apparent values only. However, in a recent paper, SHULTZ¹ calculated the ratios of the actual to apparent molecular weights and of the actual to apparent Q 's for the same trifunctionally branched polydisperse model polymer used here (Tables I and III of ref. 4). Table I shows the results for three polymers, each having an actual \bar{M}_w of 2×10^5 but with $\gamma = 0.9$ ($\bar{n}_w = 18.0$), 0.6 ($\bar{n}_w = 3.0$) and zero ($\bar{n}_w = 0$). The calculated molecular weights and Q values are in general within 10% of the actual values. These differences are considered to be within the error (arising mainly from determination of slopes required in eqn. 6) of calculating the theoretical gel permeation chromatography traces.

ANALYSIS OF THE THEORETICAL GEL PERMEATION CHROMATOGRAPHY TRACES BY THE METHOD OF DROTT

Average molecular weights and the weight average number \bar{n}_w of branch points per molecule were determined from the theoretical gel permeation chromatograms

TABLE I
ANALYSIS OF THE THEORETICAL GPC TRACES FOR POLYDISPERSE TRIFUNCTIONALLY BRANCHED POLYMERS BY THE METHOD OF SHULTZ^a

γ	Q	$10^{-4} \bar{M}_n$		$10^{-5} \bar{M}_w$		$10^{-6} \bar{M}_z$		\bar{n}_w				
		Actual	Apparent Calc. ^a	Actual	Apparent Calc. ^a	Actual	Apparent Calc. ^a	Actual	Apparent Calc. ^a	Actual	Calc. ^b	
0.90	14.00	9.98	14.51	1.40	1.70	1.73	1.89	2.10	0.738	1.61	18	18.7
0.60	4.00	3.23	3.64	5.00	5.40	5.46	1.99	0.60	0.428	0.58	3.0	2.46
0	2.00	1.83	1.83	10.0	10.8	10.8	1.98	0.30	0.29	0.29	0	—

^a From the apparent values using the correction factors in Tables I and III of ref. 4 (for $a = 0.66$).

^b Calculated from $\bar{n}_w = (3Q)_{\text{calc.}} - 6/2$ (see eqn. 8).

TABLE II

COMPARISON OF ACTUAL MOLECULAR WEIGHTS AND \bar{n}_w 'S WITH THOSE CALCULATED BY THE DROTT PROCEDURE UNDER THE ASSUMPTION THAT $\lambda_1 = \eta/M = \text{CONSTANT}$

γ	$10^{-4} \bar{Y}_n$	$[\eta]_B/[\eta]_L^a$	$[\eta]_L^b$ (dl/g)	$[\eta]_B$ (dl/g)	$10^{-4} \bar{M}_n$	$10^{-5} \bar{M}_w$	$10^{-6} \bar{M}_z$	Q	$10^4 \lambda_1$	\bar{n}_w	$10^4 \lambda_2$
0.90	1.0	0.4618	2.238	1.034	1.40	2.00	2.10	14.0	—	18.0	0.95
—	—	—	—	1.033	1.30	1.89	1.50	14.4	0.97	18.3 ^c	—
—	—	—	—	1.034	1.31	1.91	1.52	14.6	—	—	1.04
0.60	4.0	0.7778	2.238	1.741	5.00	2.00	0.600	4.00	—	3.0	0.19
—	—	—	—	1.745	5.50	1.97	0.549	3.58	0.15	2.96 ^c	—
—	—	—	—	1.740	5.46	1.97	0.561	3.61	—	—	0.18
0	10.0	1	2.238	2.238	10.00	2.00	0.300	2.00	—	0	0
—	—	—	—	2.229	11.00	2.04	0.304	1.85	-0.09	0	0

^a From Table I of ref. 14 with $a = 0.66$ and $b = 0.50$.

^b Calculated from eqn. 12 with $\bar{M}_w = 2 \times 10^5$.

^c Calculated from $\bar{n}_w = \lambda_1 \bar{M}_w$.

^d Calculation assuming $\eta_M/M = \text{constant} = \lambda_1$.

^e Calculation using $\eta_M = (1 + \lambda_2^2 M^2)^{1/2} - 1$.

by a method proposed by DROTT¹⁻³ for polydisperse branched polymers. In this method, the various molecular weight averages and the branching density are calculated from the measured intrinsic viscosity $\langle[\eta]_B\rangle$ of the whole branched polymer and the observed GPC trace by an iterative procedure. Such a procedure requires an *a priori* assumption about branch distribution function. DROTT assumes a model in which the number of branch points, n_M , is proportional to the molecular weight of the chain, *i.e.*

$$n_M/M = \text{constant} = \lambda_1 \quad (10)$$

With this assumption and using an initial trial value of the branching parameter λ_1 , the GPC trace is used to compute the intrinsic viscosity of the whole polymer by use of the equation

$$\langle[\eta]_B\rangle = K \sum_M g_M \lambda_1^{1/2} M^{1+a} W_M \quad (11)$$

The procedure is repeated by incrementing or decrementing λ_1 until the calculated intrinsic viscosity agrees with the measured value.

Since the various molecular weight averages and the weight average number \bar{n}_w of branch points per molecule are known for the theoretically calculated GPC traces, comparison of the actual values with those calculated by the DROTT procedure allows the validity of the assumption that λ_1 is constant and independent of M to be checked.

In the analysis of the theoretical GPC traces by this method, the value of $g_M \lambda_1$ required in eqn. 11 was calculated from eqn. 9 by replacing n_z by $M \lambda_1$. The intrinsic viscosities of the whole polymers are required as input to DROTT's programme. These viscosities were computed from the ratios $\langle[\eta]_B\rangle/\langle[\eta]_L\rangle$ calculated by BERGER AND SHULTZ¹⁴ for the same model polymer as employed here. $\langle[\eta]_L\rangle$ is the intrinsic viscosity of a linear chain having the same \bar{M}_w as the branched polymer but having the most probable molecular weight distribution (for which $Q = 2$). The value of $\langle[\eta]_L\rangle$ was computed by correcting the constant K in eqn. 3 for the effect of the polydispersity (since eqn. 3 applies to a monodisperse polymer). It can readily be shown for the most probable distribution that

$$\langle[\eta]_L\rangle = 0.946 K \bar{M}_w^a \quad (12)$$

where $K = 9.54 \times 10^{-4}$ dl/g and $a = 0.64$, as used for calculating the theoretical gel permeation chromatography traces. This value of $\langle[\eta]_L\rangle$ was used to calculate $\langle[\eta]_B\rangle$ from the ratios $\langle[\eta]_B\rangle/\langle[\eta]_L\rangle$, the latter being obtained from Table I of ref. 14 with $a = 0.66$ and $b = 0.50$.

Table II shows the actual molecular weight averages and those calculated by the DROTT procedure for three polymers having the same \bar{M}_w (2×10^5) but with different degrees of branching, γ values being between 0 (*i.e.* linear chain) and 0.90. The difference between the actual and calculated values is considered to be within the error involved in constructing the theoretical GPC traces. Also shown in Table II are the calculated values for λ_1 . With the linear polymer ($\gamma = 0$), a negative value for λ_1 is obtained. Since the iterative procedure ceases as soon as a negative value of

λ_1 is obtained, such a value indicates a linear chain. The final column of Table II shows the weight average number, \bar{n}_w , of branch points, the actual values being calculated from γ via eqn. 8 and the calculated values from the product of λ_1 and the calculated \bar{M}_w . Good agreement is obtained between the actual and calculated values of \bar{n}_w .

We conclude therefore, that the DROTT procedure for analysing polydisperse branched polymers provides a reliable measurement of both molecular weight averages and of \bar{n}_w , at least for polymers conforming to the STOCKMAYER distribution of molecular weights and branch points. At first sight, such a conclusion may seem surprising since the assumption that $\lambda_1 = n_M/M$ is constant applies only approximately to the STOCKMAYER distribution. Fig 5 shows a plot of n_z/Z against $Z = M/\bar{Y}_n$ for different values of γ . Although at higher values of molecular weight, constancy of n_z/Z is observed, it decreases with decreasing molecular weight at low molecular weights.

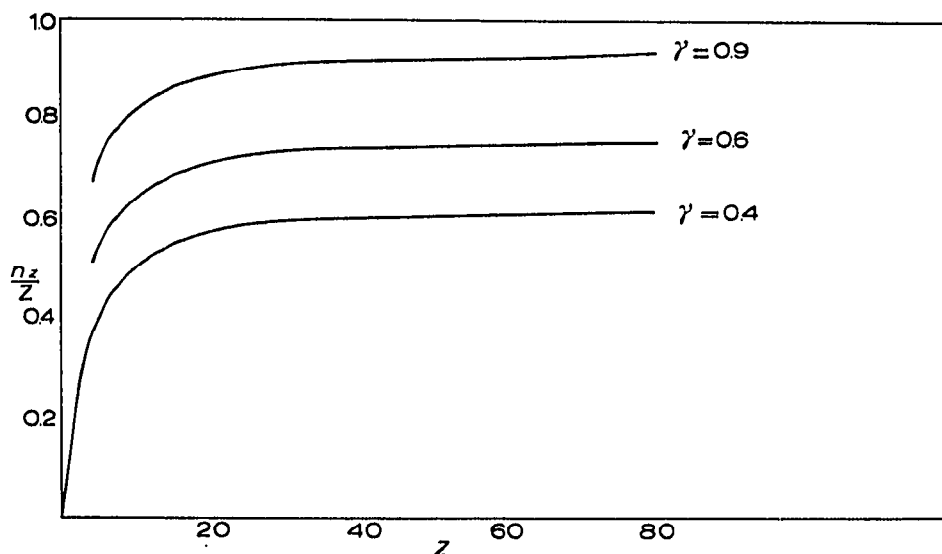


Fig. 5. Plot of the ratio n_z/Z (the average number of branch points per Z -mer to the reduced molecular weight) versus Z for three different degrees of branching.

However, the DROTT procedure for determining molecular parameters is based on the use of eqn. 11 for $\langle [\eta]_B \rangle$; this equation involves a weight averaging and consequently is relatively insensitive to the characteristics of low molecular weight species. As a result, the calculated value of λ_1 is determined mainly by the high molecular weight chains for which λ_1 is constant for the STOCKMAYER distribution. This latter conclusion was confirmed by modifying the DROTT method by replacing eqn. 10 by an equation which more accurately represents the dependence of n on M for the STOCKMAYER distribution. The equation used was⁴

$$n_M = (1 + \lambda_2^2 M^2)^{1/2} - 1 \quad (13)$$

where λ_2^2 is a constant equal to γ/\bar{Y}_n^2 . Thus λ_2 is now the branching index (in place of λ_1 in DROTT's original method) which is determined by the iterative procedure. No significant difference in the calculated average molecular weights and \bar{n}_w 's was obtained by using the more accurate eqn. 13 in place of the approximate eqn. 10 (see Table II).

Thus we may conclude that the DROTT procedure for characterising polydisperse branched polymers is fairly insensitive to the characteristics of the low molecular weight chains; reliable molecular weights and branching densities will be obtained provided that the distribution of branch points in the real polymer is such that λ_1 is constant at the higher molecular weights.

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