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PREDICTED GEL PERMEATION BEHAVIOUR OF RANDOM DISTRIBUTION POLYMERS HAVING RANDOM TRI- OR TETRA-FUNCTIONAL BRANCHING*

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Abstract—The transport behaviour of polymer chains through gel permeation columns has been observed empirically to be controlled by the hydrodynamic volumes of the chains. This observation allows one to predict the gel permeation behaviour of randomly branched, polydisperse polymers by combining existing molecular weight and branch distribution expressions with theoretical relations for the dependence of solution viscosities upon branching.

The present study comprises theoretical treatment of the GPC behaviour of polymers such as those formed by random condensations of $RA_2 + R'A_3 + R''B_2$ or $RA_2 + R'A_4 + R''B_2$ systems. The applicable Stockmayer mol. wt. and branch distribution functions are used. The Zimm–Kilb approximation to the intrinsic viscosity of branched polymer chains, $[\eta]_{br} = K g^{\frac{1}{2}} M^a$ where $g = \overline{R^2}$ (branched)/$\overline{R^2}$ (linear), is employed to relate the hydrodynamic volumes of the branched chains to those of linear chains. The assumption of a single log (hydrodynamic volume) vs. GPC elution volume relation for all the polymeric solute species permits formulation of the branched polymer GPC curve functions relative to those for linear polymer.

Integration of GPC curves for the polydisperse branched polymers, in accordance with calibration relations based upon linear polymer chains, yields apparent $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$ values. Digital computer calculations, using the expressions formulated in the present study, have generated correction factors which permit correction of these apparent mol. wt. averages to true mol. wt. averages.

INTRODUCTION

THE SEPARATION of polymer molecules by gel permeation chromatography appears to proceed according to the hydrodynamic volumes of the polymer coils.(1, 2) A "universal" GPC calibration for a given column, solvent, and temperature combination should then result in a single log ($[\eta]\cdot M$) vs. elution volume relation for all polymer molecules. This appears to be a good approximation for several linear and branched polymer systems.(1–7) Descriptions have been given of initial attempts(4, 5) to treat the effect of long-chain branching upon the GPC behaviour of polydisperse polymers, assuming direct proportionality between the number of branches and the mol. wt. of a polymer species and assuming the applicability of a "universal" log ($[\eta]\cdot M$) vs. elution volume relation. The present paper computes the expected GPC behaviour for non-fractionated, randomly branched polymers having trifunctional or tetrafunctional branch points. This introduces the effect of molecular size depression by branching upon the GPC line shape. This effect was previously commented upon with respect to polydisperse polymers having random trifunctional branching,(8) but no attempt was made to treat the effect at that time.

THEORETICAL DEVELOPMENT

The gel permeation behaviour of the polydisperse randomly branched polymers is here treated by inserting the intrinsic viscosity functions(9–12) for trifunctionally

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and tetrafunctionally branched polymers into the empirical gel permeation relation determined for linear polymers, and integrating the resulting functions over all molecular species present.

It is assumed that

$$\log([\eta]\cdot \mathrm{M}) = \xi(v) \tag{1}$$

where $\xi(v)$ is an empirically determined "universal" function of the elution volume (v) for all polymer species in the given GPC column under a given set of operating conditions.

A known viscosity–mol. wt. relation, presumably,

$$[\eta]_l = K\mathrm{M}^a \tag{2}$$

is at hand for non-branched polymer chains of the polymer of interest in the GPC solvent at the GPC column operating temperature. The use of Eqns. (1) and (2), or the knowledge of Eqn. (2) and calibration of the column with linear polymer fractions of known mol. wt. allows one to proceed with the branched polymer GPC analysis.

The ratio of the mean-square radii of gyration of the branched and linear molecules is defined as

$$g = \overline{\mathrm{R}^2}_{\mathrm{br}}/\overline{\mathrm{R}^2}_l. \tag{3}$$

The intrinsic viscosity of a randomly branched polymer molecule is, to a good approximation, related to the intrinsic viscosity of the linear polymer molecule of the same mol. wt. by (9)

$$[\eta]_{\mathrm{br}} = g^{\frac{1}{2}}\,[\eta]_l. \tag{4}$$

For simplicity in expressing the differential weight distribution functions, a reduced variable (z) is defined as

$$z = \mathrm{M}/\bar{\mathrm{M}}_{\mathrm{n}}. \tag{5}$$

$\bar{\mathrm{M}}_{\mathrm{n}}$ is the number-average mol. wt. of the polydisperse polymer in the absence of branch points, i.e. the number-average mol. wt. of the primary distribution of linear molecules.

One may then speak of the differential weight fraction W_z associated with z-mer species, and, correspondingly of the average number of branch points (n_z) possessed by a z-mer.

$$n_z = \sum_{n=0}^{\infty} n\,W_{nz}\Big/\sum_{n=0}^{\infty} W_{nz}. \tag{6}$$

For the branched polymer, the intrinsic viscosity of a z-mer may then be stated as

$$[\eta]_{\mathrm{br}} = K'\,g_z^{\frac{1}{2}}\,z^a \tag{2a}$$

where g_z is a function of n_z (cf. seq.).

The differential weight fraction observed by GPC associated with a given $\log([\eta]\cdot z)$ interval as from the "universal" calibration is

$$W_{\log([\eta]\cdot z)} = g_z^{\frac{1}{2}}\,z^{a+1}\left(\frac{\partial\,(g_z^{\frac{1}{2}}\,z^{a+1})}{\partial z}\right)^{-1} W_z \tag{7}$$

and

$$\log([\eta]\cdot z) = \log K' + \log g_z^{\frac{1}{2}} + (a+1)\log z. \tag{8}$$

If one has calibrated the GPC column with linear polymer molecules, the apparent $z(z_{\mathrm{APP}})$ of branched molecules of z units and the differential weight fraction of the polymer associated with these molecules are found by partial differentiation to be

$$z_{\mathrm{APP}} = (g_z^{\frac{1}{2}})^{1/(a+1)}\, z \tag{9}$$

$$W_{z_{\mathrm{APP}}} = (a+1)\, z^a (g_z^{\frac{1}{2}})^{a/(a+1)} \left(\frac{\partial\,(g_z^{\frac{1}{2}}\, z^{a+1})}{\partial z}\right) W_z. \tag{10}$$

The apparent number-, weight-, and z-average distribution moments for the randomly branched polydisperse polymer may be obtained by the usual integrations:

$$(\bar{z}_{\mathrm{n}})_{\mathrm{APP}} = \left(\int_0^\infty z^{-1}{}_{\mathrm{APP}}\, W_{z_{\mathrm{APP}}}\, \mathrm{d}z_{\mathrm{APP}}\right)^{-1}$$

$$= \left(\int_0^\infty (g_z^{\frac{1}{2}})^{-1/(a+1)}\, z^{-1}\, W_z\, \mathrm{d}z\right)^{-1}. \tag{11}$$

$$(\bar{z}_{\mathrm{w}})_{\mathrm{APP}} = \int_0^\infty z_{\mathrm{APP}}\, W_{z_{\mathrm{APP}}}\, \mathrm{d}z_{\mathrm{APP}}$$

$$= \int_0^\infty (g_z^{\frac{1}{2}})^{1/(a+1)}\, z\, W_z\, \mathrm{d}z. \tag{12}$$

$$(\bar{z}_z)_{\mathrm{APP}} = \int_0^\infty z^2{}_{\mathrm{APP}}\, W_{z_{\mathrm{APP}}}\, \mathrm{d}z_{\mathrm{APP}}/(\bar{z}_{\mathrm{w}})_{\mathrm{APP}}$$

$$= \int_0^\infty (g_z^{\frac{1}{2}})^{2/(a+1)}\, z^2\, W_z\, \mathrm{d}z \Big/ \int_0^\infty (g_z^{\frac{1}{2}})^{1/(a+1)}\, z\, W_z\, \mathrm{d}z. \tag{13}$$

The true distribution moments are

$$\bar{z}_n = \left(\int_0^\infty z^{-1}\, W_z\, \mathrm{d}z\right)^{-1}. \tag{14}$$

$$\bar{z}_w = \int_0^\infty z\, W_z\, \mathrm{d}z \tag{15}$$

$$\bar{z}_z = \int_0^\infty z^2\, W_z\, \mathrm{d}z \Big/ \int_0^\infty z\, W_z\, \mathrm{d}z. \tag{16}$$

We now define correction factors relating the apparent distribution moments to the true distribution moments

$$F_n = \bar{z}_n/(\bar{z}_{\mathrm{n}})_{\mathrm{APP}}. \tag{17}$$

$$F_w = \bar{z}_w/(\bar{z}_{\mathrm{w}})_{\mathrm{APP}}. \tag{18}$$

$$F_z = \bar{z}_z/(\bar{z}_z)_{\mathrm{APP}}. \tag{19}$$

In order to establish the apparent distributions indicated in Eqns. (9) and (10), and to accomplish the integrations in Eqns. (11)–(16), it is necessary to choose functions for W_z and $g_z^{\frac{1}{2}}$. The W_z functions here chosen are those derived by Stockmayer(13) and the g_z functions are those of Zimm and Stockmayer.(14)

The polydisperse polymers having randomly distributed *trifunctional* branch points have differential weight fraction distributions (in the present terminology and with only minor approximations(11) to the original(13) distribution function)

$$W_z = 2ze^{-z(\gamma+1)} \sum_{n=0}^{\infty} \frac{(\gamma z^2)^n}{n!\,(n+2)!}. \tag{20}$$

This function results from the summation over the various branched species having a total of z units and n branch points

$$W_z = \sum_{n=0}^{\infty} W_{nz}. \tag{20a}$$

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

$$W_{nz} = \frac{\gamma z^2}{n(n+2)} W_{n-1,\,z} \quad n \geq 1.$$

γ is the branching index which ranges from zero for non-branched, polydisperse polymer to unity for the polymer at incipient gelation (infinite network formation). $g_z^{\frac{1}{2}}$ is here related to n_z [Eqn. (6)] by the expression(10, 11, 14)

$$g_z^{\frac{1}{2}} \cong \{[1 + (n_z/7)]^{\frac{1}{2}} + (4n_z/9\pi)\}^{-\frac{1}{2}}. \tag{21}$$

n_z is directly computed by using Eqns. (6) and (20a). Simplification of the W_z, n_z, and $g_z^{\frac{1}{2}}$ functions at very large values of z (e.g. $z \geq 120$) to facilitate integrations has been previously described.(11, 12)

In present terminology, the differential weight distribution function for polydisperse polymers having randomly distributed *tetrafunctional* branch points is.(10, 13, 15)

$$W_z = 2ze^{-z(\frac{\gamma}{2}+1)} \sum_{n=0}^{\infty} \frac{\left(\frac{\gamma}{2} z^3\right)^n}{n!\,(2n+2)!}. \tag{22}$$

$$W_z = \sum_{n=0}^{\infty} W_{nz}. \tag{22a}$$

$$W_{0z} = ze^{-z(\frac{\gamma}{2}+1)}$$

$$W_{nz} = \frac{\gamma z^3}{2n(2n+1)(2n+2)} W_{n-1,z} \quad n \geq 1.$$

Again, γ is the branching index ranging from zero for the non-branched polydisperse polymer to unity for the polymer at incipient gelation. The relation here used for $g_z^{\frac{1}{2}}$ is(9, 10, 14)

$$g_z^{\frac{1}{2}} \cong [(1 + n_z/6)^{\frac{1}{2}} + 4n_z/3\pi]^{-\frac{1}{2}}. \tag{23}$$

n_z is directly computed using Eqns. (6) and (22a). Simplification of the W_z, n_z, and $g_z^{\frac{1}{2}}$ functions at very large z values has been previously described.(10)

COMPUTATIONS

The apparent, GPC-observed z_{APP} and differential weight distribution functions [Eqns. (9) and (10)] and the apparent and true number-, weight-, and z-average distribution moments [Eqns. (11) through (16)] were computed for the random tri- and tetra-functionally branched polydisperse polymers. Thirteen values of the branching index γ (0–0·96) and three values of the viscosity–molecular weight exponent a (0·50, 0·66 and 1·00) were used for each of the two branching types. A GE265 digital computer with FORTRAN language programming was used in the numerical integrations of Eqns. (11)–(13). The computing techniques were similar to those employed in the branched polymer viscosity treatment.[11] Although some direct computation of the integrals Eqns. (14)–(16) was done to check programme validity, it should be noted that these distribution moments are simply expressed as: trifunctional branching:

$$\bar{z}_n = 1/\left(-\frac{\gamma}{3}\right). \tag{14a}$$

$$\bar{z}_w = 2/(1-\gamma). \tag{15a}$$

$$\bar{z}_z = 3\left(1-\frac{\gamma}{3}\right)/(1-\gamma)^2 \tag{16a}$$

tetrafunctional branching:

$$\bar{z}_n = 1/\left(1-\frac{\gamma}{4}\right). \tag{14b}$$

$$\bar{z}_w = 2/(1-\gamma). \tag{15b}$$

$$\bar{z}_z = 3/(1-\gamma)^2. \tag{16b}$$

RESULTS AND DISCUSSION

Application of the theoretical approach and computations just outlined allows a more quantitative view of the intuitively expected GPC behaviour of randomly branched polydisperse polymers. Figure 1 shows a comparison of the actual (broken line) with the apparent (solid line) mol. wt. distribution one would compute from a gel permeation chromatogram of a polydisperse polymer having randomly distributed trifunctional branch points ($\gamma = 0{\cdot}8$) examined under theta conditions ($a = 0{\cdot}50$). The column is assumed to have been calibrated with linear molecules of the polymer in question. The branching "sharpens" the apparent distribution by the progressive shifting of branched high mol. wt. polymer species to lower apparent mol. wt. Computation of average mol. wts. by numerical integration of the curves in Fig. 1 yields (cf. Table 3):

$F_n = \bar{z}_n/(\bar{z}_n)_{\mathrm{APP}} = 1{\cdot}018$, $F_w = \bar{z}_w/(\bar{z}_w)_{\mathrm{APP}} = 1{\cdot}322$, and $F_z = \bar{z}_z/(\bar{z}_z)_{\mathrm{APP}} = 1{\cdot}796$.

Thus, although the distortion of the distribution curve may not appear excessive in Fig. 1, a weight-average mol. wt. computed from the GPC curve, ignoring the branching effect, would be only about 76 per cent of the true $\bar{M}_w$. The discrepancy, of course, increases with increasing γ.

Tables 1–4 present the results of integrating Eqns. (11)–(16). Tables 1 and 2 may be used to ascertain γ for the respective branched systems and then Tables 3 and 4 may be

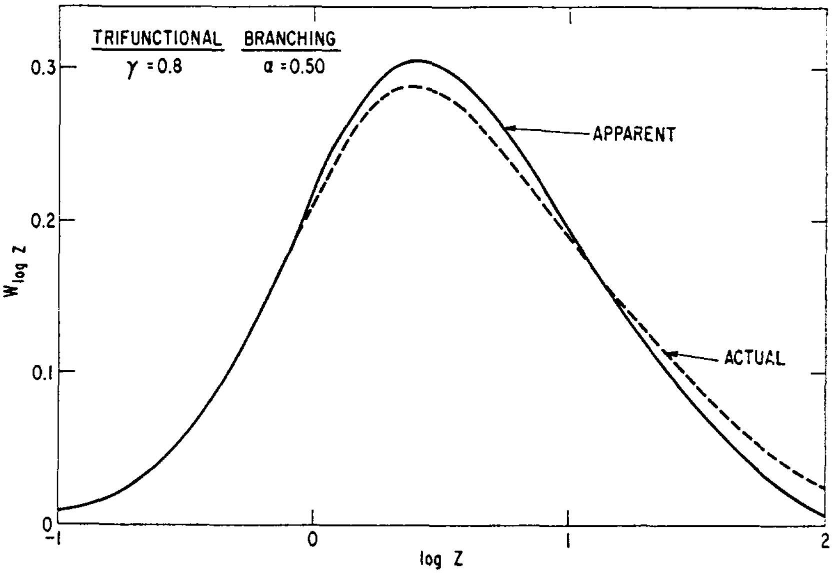

FIG. 1. Apparent and actual differential weight distribution curves for a trifunctionally branched, polydisperse polymer. Branching index $\gamma = 0{\cdot}8$. The GPC solvent and temperature are assumed to be at theta condition ($a = 0{\cdot}50$). The GPC calibration from which the apparent distribution was computed was accomplished with linear polymer molecules.

TABLE 1. ACTUAL AND APPARENT RATIOS OF DISTRIBUTION MOMENTS AT SEVERAL VALUES OF THE BRANCHING INDEX; POLYDISPERSE POLYMER WITH RANDOMLY DISTRIBUTED TRIFUNCTIONAL BRANCH POINTS

		$a = 0{\cdot}50$	$a = 0{\cdot}66$	$a = 1{\cdot}00$
γ	$\bar{z}_w/\bar{z}_n$	$(\bar{z}_w)_{APP}/(\bar{z}_n)_{APP}$	$(\bar{z}_w)_{APP}/(\bar{z}_n)_{APP}$	$(\bar{z}_w)_{APP}/(\bar{z}_n)_{APP}$
0·0	2·0000	2·0000	2·0000	2·0000
0·1	2·1482	2·1216	2·1240	2·1282
0·2	2·3333	2·2711	2·2769	2·2862
0·3	2·5714	2·4592	2·4694	2·4862
0·4	2·8889	2·7029	2·7196	2·7469
0·5	3·3333	3·0324	3·0594	3·1030
0·6	4·0000	3·5061	3·5492	3·6199
0·7	5·1111	4·2534	4·3251	4·4462
0·8	7·3333	5·644	5·7791	6·0105
0·9	14·0000	9·263	9·6257	10·236
0·92	17·3333	10·865	11·351	12·165
0·94	22·8889	13·341	14·031	15·196
0·96	34·0000	17·716	18·890	20·782

used to obtain the factors [Eqns. (17) to (19)] with which to correct the apparent $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_z$, computed from GPC ignoring branching, to the true $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_z$ values.

Figure 2 is a representation of the actual $\bar{z}_w/\bar{z}_n$ ratios in the randomly branched polydisperse polymers plotted against the apparent $\bar{z}_w/\bar{z}_n$ ratios computed from gel permeation chromatograms [under theta conditions, i.e. $a = 0{\cdot}50$ in Eqn. (2)] ignoring

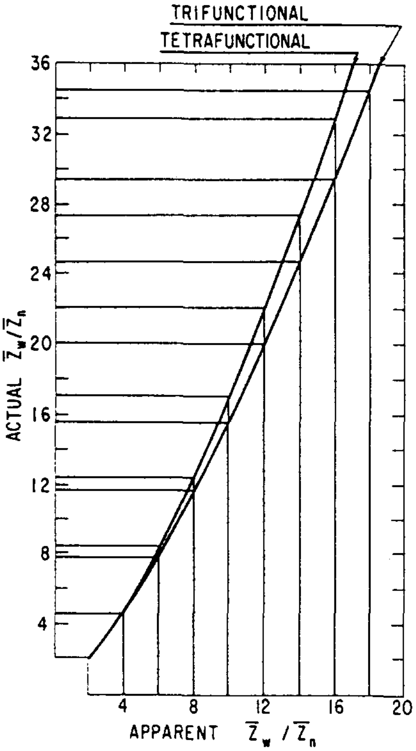

FIG. 2. Actual distribution moment ratios ($\bar{z}_w/\bar{z}_n$) plotted against apparent ($\bar{z}_w/\bar{z}_n$) computed by ignoring the branching effect on polymer coil volumes. Both random tri- and tetra-functionally branched, polydisperse polymers are represented. Theta solvent conditions are here assumed (a = 0·50).

TABLE 2. ACTUAL AND APPARENT RATIOS OF DISTRIBUTION MOMENTS AT SEVERAL VALUES OF THE BRANCHING INDEX; POLYDISPERSE POLYMER WITH RANDOMLY DISTRIBUTED TETRAFUNCTIONAL BRANCH POINTS

γ	$\bar{z}_w/\bar{z}_n$	$a = 0{\cdot}50$ $(\bar{z}_w)_{APP}/(\bar{z}_n)_{APP}$	$a = 0{\cdot}66$ $(\bar{z}_w)_{APP}/(\bar{z}_n)_{APP}$	$a = 1{\cdot}00$ $(\bar{z}_w)_{APP}/(\bar{z}_n)_{APP}$
0·0	2·000	2·000	2·000	2·000
0·1	2·167	2·127	2·131	2·137
0·2	2·375	2·286	2·294	2·307
0·3	2·659	2·485	2·499	2·523
0·4	3·000	2·742	2·765	2·803
0·5	3·500	3·089	3·124	3·183
0·6	4·250	3·583	3·639	3·732
0·7	5·500	4·356	4·450	4·606
0·8	8·000	5·802	5·944	6·238
0·9	15·50	9·383	9·820	10·57
0·92	19·25	10·97	11·54	12·54
0·94	25·50	13·40	14·20	15·61
0·96	38·00	17·68	18·94	21·20

the effect of branching. At $\gamma = 0$ there exists $\bar{z}_w/\bar{z}_n = 2{\cdot}0$ characteristic of the most probable mol. wt. distribution for polydisperse linear polymers. With branching broadening of the distributions the apparent distribution moment ratios $(\bar{z}_w)_{APP}/(\bar{z}_n)_{APP}$, obtained by straightforward evaluation of the GPC traces ignoring branching,

TABLE 3. DISTRIBUTION MOMENT CORRECTION FACTORS; POLYDISPERSE POLYMER WITH RANDOMLY DISTRIBUTED TRIFUNCTIONAL BRANCH POINTS

	$a = 0·50$			$a = 0·66$			$a = 1·00$		
γ	F_n	F_w	F_z	F_n	F_w	F_z	F_n	F_w	F_z
0·0	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000
0·1	1·002	1·015	1·051	1·002	1·013	1·031	1·002	1·011	1·026
0·2	1·005	1·032	1·075	1·004	1·029	1·068	1·003	1·024	1·056
0·3	1·007	1·053	1·125	1·006	1·048	1·113	1·005	1·040	1·094
0·4	1·009	1·079	1·189	1·008	1·071	1·170	1·007	1·059	1·140
0·5	1·012	1·112	1·272	1·010	1·101	1·244	1·009	1·083	1·200
0·6	1·014	1·157	1·387	1·012	1·141	1·345	1·010	1·116	1·282
0·7	1·016	1·221	1·547	1·014	1·198	1·485	1·012	1·163	1·392
0·8	1·018	1·322	1·796	1·016	1·289	1·699	1·013	1·236	1·556
0·9	1·018	1·539	2·359	1·017	1·479	2·176	1·014	1·386	1·912
0·92	1·019	1·625	2·589	1·017	1·553	2·367	1·014	1·444	2·050
0·94	1·019	1·747	2·916	1·017	1·659	2·635	1·014	1·527	2·242
0·96	1·019	1·955	3·423	1·017	1·830	2·948	1·014	1·658	2·534

TABLE 4. DISTRIBUTION MOMENT CORRECTION FACTORS; POLYDISPERSE POLYMER WITH RANDOMLY DISTRIBUTED TETRAFUNCTIONAL BRANCH POINTS

	$a = 0·50$			$a = 0·66$			$a = 1·00$		
γ	F_n	F_w	F_z	F_n	F_w	F_z	F_n	F_w	F_z
0·0	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000
0·1	1·002	1·021	1·058	1·002	1·019	1·053	1·001	1·015	1·044
0·2	1·004	1·043	1·121	1·004	1·039	1·104	1·003	1·032	1·091
0·3	1·006	1·070	1·196	1·005	1·063	1·177	1·004	1·039	1·146
0·4	1·008	1·102	1·288	1·007	1·092	1·259	1·006	1·077	1·213
0·5	1·009	1·144	1·404	1·008	1·130	1·361	1·007	1·107	1·295
0·6	1·011	1·199	1·558	1·010	1·179	1·496	1·008	1·148	1·401
0·7	1·012	1·278	1·771	1·011	1·250	1·679	1·009	1·205	1·542
0·8	1·013	1·405	2·103	1·012	1·362	1·962	1·010	1·295	1·755
0·9	1·014	1·675	2·818	1·012	1·598	2·555	1·010	1·481	2·185
0·92	1·014	1·779	3·095	1·012	1·689	2·782	1·010	1·551	2·344
0·94	1·014	1·930	3·491	1·012	1·818	3·100	1·010	1·650	2·563
0·96	1·014	2·180	4·147	1·012	2·031	3·620	1·010	1·811	2·913

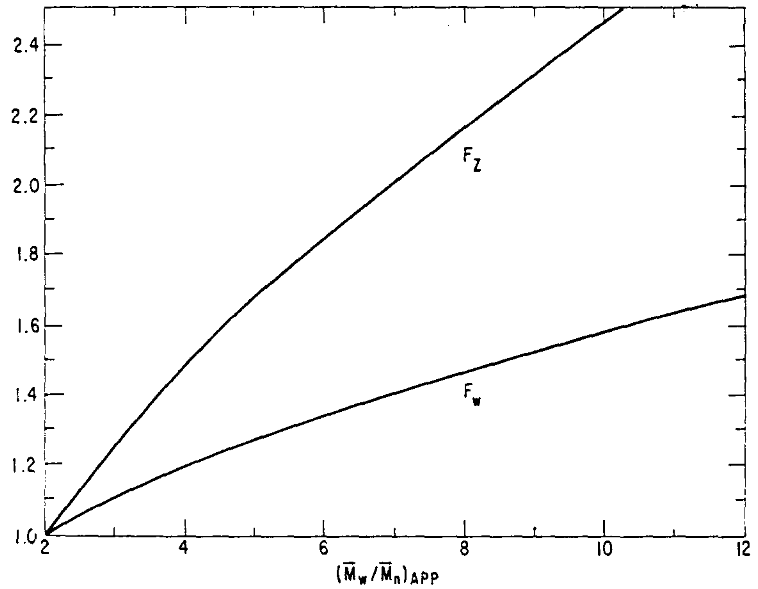

FIG. 3. Correction factors for apparent weight-average and z-average moments plotted against the apparent weight-average to number-average moment ratio for random trifunctionally branched, polydisperse polymers ($a = 0 \cdot 50$).

progressively fall farther and farther below the true ratios. The effect is slightly greater, on this basis, for the tetrafunctionally branched systems, but considerable correspondence is maintained to fairly high branching indices. A plot such as Fig. 2 permits one to proceed directly to the correction factors F_w and F_z by use of plots such as Fig. 3 for random trifunctionally branched polymers with $a = 0 \cdot 50$. Alternatively, empirical mathematical expressions relating the quantities shown in Tables 1–4 may be generated to allow interpolation for various γ and a combinations. It will here only be further remarked that the tabulated quantities and $\bar{z}_n$, $\bar{z}_w$, and $\bar{z}_z$ values readily computed by Eqns. (14a), (15a) and (16a) or Eqns. (14b), (15b) and (16b) can be used for complete tabulation of the three apparent distribution moments for the given γ and a pairs.

A brief comparison of the present mathematical treatment of these branched systems with the treatment by Drott[(4, 5)] of similar systems is in order. The present approach assigns definite distribution functions to the branched polymer systems. These are distributions which can be obtained by random condensation of $RA_2 + R'A_3 + R''B_2$ systems (random trifunctionally branched polydisperse polymers) or $RA_2 + R'A_4 + R''B_2$ systems (random tetrafunctionally branched polydisperse polymers). The former may also be approximately achieved by free radical polymerization with chain transfer to polymer. The latter can be achieved by random cross-linking of a most probable distribution of linear polymer molecules, and approximately achieved by free radical polymerization of vinyl + divinyl monomer systems. In any case, the mol. wt. distributions and branch distributions are specified and lead to definite interrelations of physical quantities of interest. The branching model assumed by Drott[(4, 5)] specifies that the number of branch points per molecule is directly

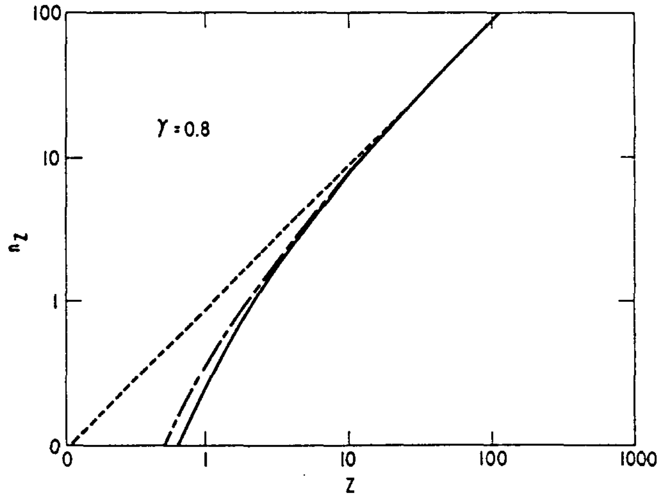

FIG. 4. The average number of trifunctional branch points, n_z, per z-mer plotted against z (log–log scale for *a* randomly branched polydisperse polymer at branching index $\gamma = 0 \cdot 8$. ———— Actual n_z; —— — —— $n_z \cong (1 + \gamma z)^{\frac{1}{2}} - 1$; —— —— —— —— $n_z \approx \gamma^{\frac{1}{2}} z$.

proportional to the number of units in the molecule. The branch density is then arrived at by iterative treatment of the observed GPC data, and intrinsic viscosity data on the whole polymer.(4) A similar procedure is applied to the intrinsic viscosity and GPC data of polymer fractions.(5) The specification that the ratio of the number of branch points to mol. wt. is constant for species in the polydisperse polymer(4, 5) is actually as restrictive as, and in a sense more arbitrary than, the specification of definite, plausible mol. wt. and branch distribution functions in the present study. The two approaches must lead to fairly comparable results at high branching density, i.e., as $\gamma \longrightarrow 1$ in the present terminology. Figure 4 depicts the actual (solid curve) relation and two approximate relations between the number of branch points per z-mer n_z and z in the polydisperse polymer with random trifunctional branching at $\gamma = 0 \cdot 8$. The three relations shown are

$$n_z = \sum_{n=0}^{\infty} n\, W_{nz} / \sum_{n=0}^{\infty} W_{nz} \tag{6}$$

$$n_z \cong (1 + \gamma z^2)^{\frac{1}{2}} - 1 \tag{24}$$

$$n_z \approx \gamma^{\frac{1}{2}} z. \tag{25}$$

As can be seen in Fig. 4, Eqn. (24) is a rather good approximation to the true expression, Eqn. (6), but Eqn. (25) approximates the n_z vs. z relation well only at high z values. Since, however, the viscosity and GPC functions are most sensitive to the high mol. wt. highly branched polymer species, correct application of the iterative Drott(4) procedure on such a system should yield a result $n_z/z \simeq \gamma^{\frac{1}{2}}$ as an estimate of the branching index in random trifunctionally branched polymers. In random tetrafunctionally branched polymers, the iterative procedure should yield $n_z/z \simeq \gamma^{1/3}/2$ as an estimate of the branching index [cf. Ref. 10, Eqn. (13)].

In conclusion, the present study places on a more quantitative basis the prediction of GPC behaviour of randomly branched, polydisperse polymer systems. It provides correction factors which may be used to convert apparent average mol. wts. of súch systems, computed from GPC data using linear molecule calibration curves, to the true average mol. wts. The approach used is reasonably flexible and amenable to modification if a different formal relationship between GPC elution behaviour and polymer coil dimensions should prove more satisfactory.

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