

SOLUTION PROPERTIES OF BRANCHED POLYMERS. II.*

DETERMINATION OF THE DEGREE OF BRANCHING OF POLYDISPERSE BRANCHED POLYMERS

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An investigation was made of the dependence of the intrinsic viscosity of the branched polydisperse methyl methacrylate-ethylene dimethacrylate (0.25–1.0 mol.%) copolymers on the content of the branching agent and the thermodynamic quality of the solvent. The possibilities of determination of the degree of branching of polydisperse branched polymers are discussed on the basis of a critical analysis of the results.

In the paper¹, we have pointed out the problems involved in the characterization of branched polydisperse systems on the basis of the physicochemical properties of their solution or solutions of their fractions; the properties under investigation were molecular weight, intrinsic viscosity and radius of gyration. The most sensitive parameter is the ratio of the intrinsic viscosities of a branched and a linear polymer having the same molecular weight, because the decrease in the intrinsic viscosity that accompanies branching is quite considerable. Moreover, the measurement is not time-consuming (in contrast with fractionation and characterization of fractions). The dependence of the intrinsic viscosity of a branched polymer, $[\eta]_b$, on the weight average molecular weight, M_w , (or degree of polymerization, P_w) is affected not only by the degree of branching, but also by the polydispersity of molecular weights, increasing with the growing degree of branching. A comparison of $[\eta]_b$ with the intrinsic viscosity of a linear polymer, $[\eta]_l$, having the common distribution of molecular weights ($M_w/M_n \sim 2$) gives only a semiquantitative idea of the degree of branching. To obtain an exact value of the degree of branching, the branched polymer should be compared with a hypothetical linear polymer having the distribution of molecular weights of the same type and width as the branched polymer. To calculate the viscosity of a hypothetical linear polymer the knowledge of the distribution function of molecular weights of the branched polymer is needed. For branched systems having tetra- and polyfunctional branch units, there exists only the distribution function² on the assumption that all the double bonds in the polymerizing system have the same reactivity and no intramolecular rings are formed. No generalization involving the effect of different reactivities of the double bonds and intramolecular cyclization on distribution has as yet been given. However, since even in systems not fulfilling Stockmayer's assumptions² his distribution describes with sufficient accuracy the experimentally determined molecular weight distribution¹, we used it as a basis for the calculations of the correction factors and the ratio $[\eta]_b/[\eta]_l$. A simplified form of the weight differential distribution function was used³, for small amounts of randomly occurring tetrafunctional units in the chain:

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$$W_x = \sum_{n=0}^{\infty} W_{n,x} = 2x \exp\left(-x\left(\frac{\gamma}{2} + 1\right)\right) \sum_{n=0}^{\infty} \frac{(x^3\gamma)^n}{2^n n! (2n+2)!}; \quad (1)$$

here, n is the number of tetrafunctional units in the chain, $x = 2P/P_{w,0}$, the relative degree of polymerization, $\gamma = 1 - P_{w,0}/P_w$ the degree of branching², P the degree of polymerization, $P_{w,0}$ its weight average value for the so-called primary chain³, and P_w its weight average value for the branched polymer. According to Zimm and Stockmayer⁴, the intrinsic viscosities and mean square radii of gyration of the branched (\overline{S}_b^2) and the linear (\overline{S}_l^2) monodisperse polymer are related with each other by

$$[\eta]_b/[\eta]_l = (\overline{S}_b^2/\overline{S}_l^2)^b = b^b. \quad (2)$$

The value of the exponent b still remains an object of theoretical and experimental study. Zimm and Kilb⁵, on the basis of theoretical reasonings, regard $b = 0.5$ as a universally satisfying value for the Θ -conditions. On the other hand, Berry⁶ believes b to be dependent on the mutual order (topology) of chains in the branched macromolecule, particularly on the type of the branch units. A no less controversial problem consists in the dependence of the exponent b on the thermodynamic quality of the solvent with respect to the polymer under investigation. From the so far acknowledged theory of the volume effects of branched macromolecules⁷ it follows that the exponent b decreases with the thermodynamic improvement of the medium with respect to the polymer. In the published theoretical papers dealing with the problem of the hydrodynamic behaviour of simple branched or cyclic models, the above tendency⁸ is described along with the opposite phenomenon⁹, *i.e.* the growth of the exponent b with the increasing thermodynamic quality of the solvent. Experimentally, only the growth of b was determined, but the branched systems studied were polydisperse^{10,11}. However, Bloomfield and Sharp¹² assume, on the basis of their own calculations, that the transition from the Θ -solvents to thermodynamically better solvents leads to a relatively identical change in the hydrodynamic behaviour of all types of chains (regardless of topology); that is, b does not change.

In the present communication, values were calculated of the ratio $[\eta]_b/[\eta]_l$ corrected for polydispersity for several media differing in their solvent power (*i.e.* for various values of the Mark-Houwink equation exponent a) and for various values of the exponent b ; a comparison of theoretical and experimental values is used to discuss what information, and under what conditions, may be obtained on the basis of the intrinsic viscosity of polydisperse branched polymers.

EXPERIMENTAL

Materials. Preparation and more detailed characterization of the branched polydisperse copolymers of methyl methacrylate with ethylene dimethacrylate (0.25, 0.50, 0.75, 1.00 mol% with respect to methyl methacrylate in the initial polymerization mixture) have been described in a preceding communication¹. Dioxan, butyl acetate and ethyl acetate used were dried and distilled.

Measurements. The light scattering measurements were carried out with a Photo-Gonio-Diffusomètre Sofica apparatus. The measuring technique and data treatment have been described earlier¹. The refractive index increments dn/dc and constants A for calculation of the size of polydisperse linear poly(methyl methacrylate) having a normal distribution in the individual solvents are given below (Table III). The experimental technique of viscometric measurements has been described in the communication¹. The constants of the Mark-Houwink equation for poly(methyl methacrylate) in the solvents used are given below (Table III).

TABLE I
Values of the Correction Factors Q_1

γ	$a = 0.5$	$a = 0.6$	$a = 0.75$	γ	$a = 0.5$	$a = 0.6$	$a = 0.75$
0.0	0.9400	0.9440	0.9560	0.6	0.8321	0.8349	0.8721
0.1	0.9297	0.9260	0.9457	0.7	0.7948	0.7952	0.8418
0.2	0.9163	0.9330	0.9376	0.8	0.6894	0.7432	0.7970
0.3	0.9014	0.8991	0.9258	0.9	0.6393	0.6466	0.7331
0.4	0.8831	0.8823	0.9177	0.95	0.5409	0.5526	0.6346
0.5	0.8611	0.8583	0.8943				

TABLE II
Values of the Correction Factors Q_b/Q_1

b	a	$\gamma: 0.1$	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.95
0.4	0.50	0.9818	0.9654	0.9480	0.9282	0.9041	0.8756	0.8404	0.8360	0.7198	0.5688
	0.60	0.9880	0.9498	0.9500	0.9265	0.9022	0.8661	0.8291	0.7723	0.6860	0.6080
	0.75	0.9814	0.9589	0.9360	0.9098	0.8790	0.8405	0.7943	0.7298	0.6125	0.5370
0.5	0.50	0.9779	0.9548	0.9363	0.9120	0.8834	0.8496	0.8084	0.8077	0.6708	0.5206
	0.60	0.9838	0.9416	0.9372	0.9090	0.8798	0.8373	0.7933	0.7283	0.6313	0.5459
	0.75	0.9767	0.9495	0.9216	0.8935	0.8551	0.8101	0.7545	0.6805	0.5525	0.4672
0.6	0.50	0.9742	0.9510	0.9252	0.8967	0.8638	0.8253	0.6901	0.7694	0.6280	0.4796
	0.60	0.9796	0.9336	0.9248	0.8922	0.8581	0.8104	0.7605	0.6889	0.5841	0.4942
	0.75	0.9720	0.9403	0.9057	0.8710	0.8287	0.7785	0.7167	0.6357	0.5009	0.4101
0.7	0.50	0.9705	0.9437	0.9143	0.8821	0.8452	0.8024	0.7511	0.7347	0.5902	0.4446
	0.60	0.9755	0.9258	0.9130	0.8761	0.8383	0.7853	0.7301	0.6532	0.5427	0.4505
	0.75	0.9674	0.9314	0.8943	0.8530	0.8056	0.7502	0.6827	0.5958	0.4565	0.3633
0.8	0.50	0.9668	0.9366	0.9038	0.8680	0.8274	0.7888	0.7257	0.7030	0.5568	0.4145
	0.60	0.9715	0.9181	0.9013	0.8607	0.8180	0.7617	0.7021	0.6209	0.5065	0.4137
	0.75	0.9629	0.9226	0.8813	0.8355	0.7838	0.7237	0.6516	0.5601	0.4184	0.3245
1.0	0.50	0.9546	0.9229	0.8836	0.8414	0.7945	0.7414	0.6799	0.6477	0.5010	0.3661
	0.60	0.9636	0.9034	0.8793	0.8316	0.7818	0.7188	0.6521	0.5649	0.4469	0.3555
	0.75	0.9539	0.8985	0.8566	0.8032	0.7436	0.6759	0.5966	0.4990	0.3566	0.2652
1.5	0.60	0.9449	0.8694	0.8298	0.7684	0.7056	0.6133	0.5550	0.4621	0.3464	0.2630

RESULTS AND DISCUSSION

Calculations of the Correction Factors for Polydispersity and of the Viscosity Ratios

If we adapt the Mark-Houwink equation in agreement with relationship (2), the intrinsic viscosity of a monodisperse branched polymer is then given by

$$[\eta]_b = K g^b P^a. \quad (3)$$

For a polydisperse branched system it holds^{1,3}

$$[\eta]_b = K(P_w/2)^a (1 - \gamma)^a \int_0^\infty g_x^b x^a W_x dx = K P_w^a Q_b, \quad (4)$$

where

$$g_x = \sum_{n=0}^{\infty} g(n) W_{n,x} / \sum_{n=0}^{\infty} W_{n,x} \cong [(1 + n_x/6)^{1/2} + 4n_x/3]^{-1/2} \quad (5)$$

represents an average value of the parameter g for molecules having the relative degree of polymerization x ; it is a function of the number average number of branch units, n_x , in a fraction of the branched polymer having the relative degree of polymerization x and a statistic distribution of branches in the macromolecule⁴. The intrinsic viscosity of a hypothetical linear polymer having the same distribution as a branched polymer follows from Eq. (4) for $b = 0$. The ratios

$$[\eta]_b/[\eta]_l = \frac{\int_0^\infty g_x^b x^a W_x dx}{\int_0^\infty x^a W_x dx} = \frac{Q_b}{Q_l} \quad (6)$$

were calculated for various combinations of the values of the exponent a , parameter γ and the exponent b with a Gier computer using numerical integration according to Simpson in the region $0 \leq x \leq 91$; for higher values of x ($91 \leq x \leq \infty$), an incomplete gamma function was used^{13,14}. The calculated factors Q_l in dependence on a and γ are summarized in Table I; the ratios of the intrinsic viscosities or of the viscosity factors Q_b/Q_l are listed in Table II.

Dependence of the Intrinsic Viscosity on the Degree of Branching

The comparison of the experimental dependences obtained here with those calculated on the basis of Stockmayer's theory of distribution of branched polymers² and Zimm's and Kilb's theory of the intrinsic viscosity of branched polymers⁵ can best be represented by plotting the ratios $[\eta]_b/[\eta]_l$ as a function of $(1 - \gamma)$. (According to Zimm, Stockmayer and Thurmond^{3,4}, the value of $(1 - \gamma)$ is just equal to the z -average

of the ratio of square radii of gyration of the linear and branched polymers, g_z .) Dependences of $[\eta]_b/[\eta]_l$ on $(1 - \gamma)$, calculated for various combinations of the exponents a and b (Table II) and represented in the logarithmic coordinates are in all cases linear (Fig. 1) and can therefore be described by an empirical relationship

$$[\eta]_b/[\eta]_l = (1 - \gamma)^{f(a,b)} = g_z^{f(a,b)}, \quad (7)$$

where the exponent $f(a, b)$ depends on the values of the exponents a and b (Fig. 2). The latter plot may be used with advantage for a quick reading-off of the exponent b when determining γ with more precision as will be mentioned in the conclusion. We carried out an experimental investigation of the course of the dependences $[\eta]_b : [\eta]_l$ vs $(1 - \gamma)$ for polymers containing various amounts of the branching agent (in a given solvent) and of the effect of the quality of the solvent on these dependences (for a given content of the branching agent). The expression for calculation of the intrinsic viscosity of a hypothetical linear polymer $[\eta]_l$ is analogous to Eq. (4); only Q_b is replaced by the values of Q_l from Table I.

Effect of the Amount of the Branching Agent on $[\eta]_b$

All experimental dependences of the ratio $[\eta]_b/[\eta]_l$ on $(1 - \gamma)$ for polymers having various contents of the branching agent, if plotted logarithmically, are linear in prin-

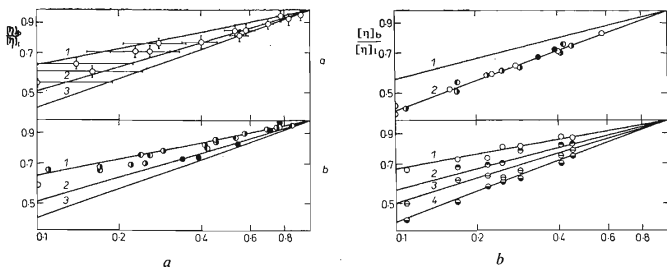


FIG. 1

Calculated and Experimental Dependences of the Ratio $[\eta]_b/[\eta]_l$ on the Degree of Branching γ

The calculations (straight lines) are based on relationship (7). (*a, b*) for $a = 0.6$, (*c*) for $a = 0.75$; *b*: 1 0.5, 2 0.8, 3 1.0; concentration of ethylene dimethacrylate, $[II]_0$ (mol% with respect to methyl methacrylate in the initial polymerization mixture): ● 0.25, ○ 0.50, ⊙ 0.75, ⊚ 1.00 (butyl acetate (*a, b*) or 1,4-dioxan (*c*) as solvents, resp.). (*d*) Calculated dependences: 1 $a = 0.5$; $b = 0.5$, 2 0.75, 0.5, 3 0.5, 0.8, 4 0.75, 0.8; experimental points for various solvents ($[II]_0 = 1$ mol%): ○ 1,4-dioxan-water (17 vol. %), ● butyl acetate, ⊖ ethyl acetate, ⊚ 1,4-dioxan.

ciple, in accordance with relationship (7) (Figs 1a, 1b). It is obvious, however, that they do not satisfy the theoretical dependences for $b = 0.5$, although Kilb¹⁴ regards this value as generally valid. The experimental points in Figs 1a,b indicate that the exponent b decreases in butyl acetate (that is, in a thermodynamically not too good solvent) with increasing content of ethylene dimethacrylate in the copolymer. The measurement of the degree of branching, γ , particularly for $\gamma \rightarrow 1$, is subject to a considerable error (experimental errors of γ and of the ratio $[\eta]_b/[\eta]_l$ are shown in Fig. 1a); we believe, however, that the observed dependence of b on the ethylene dimethacrylate content is a real one. The existence of this dependence means that the expansion of branched macromolecules in thermodynamically not too good solvents depends on their topology represented in this case by the number of the branching centres per a certain length of the chain. The change in b with the content of the branching agent indicates that the molecules of the copolymer having a higher content of the branching agent expand more (have higher values of the ratio $[\eta]_b : [\eta]_l$; this effect may be explained in terms of simple steric concepts). On the contrary, the ratios measured in a thermodynamically very good solvent – 1,4-dioxan – obey satisfactorily the theoretical dependence for $b = 0.8$, regardless of the content of the branching agent (Fig. 1c). It seems, therefore, that in thermodynamically good solvents, where the molecules are strongly expanded, the degree of their expansion is not affected by steric hindrances.

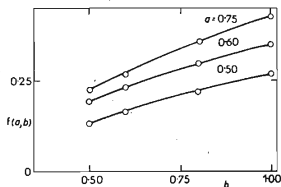


FIG. 2

Dependence of the Exponent $f(a, b)$ of Eq. (7) on the Exponents of the Mark-Houwink Equation, a , and Eq. (2), b

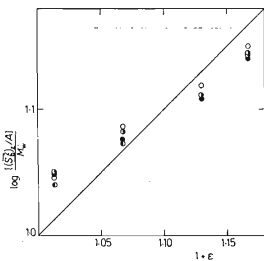


FIG. 3

Dependence of $\log \left[\frac{(\overline{S_z^2})_z}{A} \right] / \log M_w$ on $(1 + \epsilon)$

Polymers: \circ $M_w = 9.2 \cdot 10^5$, $\gamma = 0.75$; \bullet $M_w = 10.1 \cdot 10^5$, $\gamma = 0.75$; \ominus $M_w = 10.5 \cdot 10^5$, $\gamma = 0.78$; \blacksquare $M_w = 13.5 \cdot 10^5$, $\gamma = 0.83$. ϵ : 0.013 for 1,4-dioxan-water (17% by vol.), 0.067 for butyl acetate, 0.133 for ethyl acetate and 0.167 for 1,4-dioxan.

Effect of the Solvent on $[\eta]_b$

The thermodynamic quality of the solvent (at a constant content of the branching agent) affects the dependences $[\eta]_b/[\eta]_l$ vs $(1 - \gamma)$ in such a way (Fig. 1d) that with improving quality of the solvent (increasing exponent a), the value of the exponent b also increases. (To avoid possible misunderstanding, it should be noted that the straight lines in Fig. 1d are not dependences plotted through the experimental points, but theoretical dependences for combinations of the extreme values of the exponents a and b which appear in the present work; straight line 1 approximately describes the behaviour of the branched polymer in 1,4-dioxan with 17% of water, straight line 4 corresponds to the behaviour of the branched polymer in dioxan.) The following explanation seems acceptable: In thermodynamically poorer solvents, the branched molecules expand comparatively more in comparison with the linear ones, probably because the higher density of segments in a branched macromolecule (particularly in the surroundings of their centre of gravity) makes a great number of conformations sterically unrealizable, thus leading to its relatively larger expansion. This sterical factor plays then a less important part in the case of molecules already strongly expanded owing to an interaction of the branched polymer with the solvent. The conclusions from an investigation of the effect of the solvent quality are thus consistent with those following from an investigation of the effect of the content of the branching agent.

Effect of the Solvent on the Radius of Gyration

Some information about the expansion of branched macromolecules may also be obtained by measuring their sizes in a number of solvents having different thermodynamic quality, using the light scattering method. Kilb¹⁴ has shown that linear polymers having the most probable (normal) distribution of molecular weights have in the Θ -solvents the same dependence of the z -average of the mean square radius of gyration $(\overline{S_{l,\theta}^2})_z$ on the weight average molecular weight M_w as the polydisperse branched polymers obeying Stockmayer's distribution, because a decrease in $(\overline{S_{b,\theta}^2})_z$ caused by branching is just compensated for by an increase in polydispersity with the growing degree of branching. It holds in the Θ -solvents, therefore,

$$(\overline{S_{b,\theta}^2})_z = (\overline{S_{l,\theta}^2})_z = A_\theta M_w \quad (8)$$

If the expansion factor α of both linear and branched molecules were the same, it should be

$$(\overline{S_{b,z}^2})/(\overline{S_{l,z}^2}) = (\overline{S_{b,\theta,z}^2})/AM_w^{1+\epsilon} = 1, \quad (9)$$

where the factor ϵ , correcting the dependence $(\overline{S_z^2})$ against M_w for the volume effect in a thermodynamically good solvent, is related to the exponent a in the Mark-

Houwink equation (for the same solvent) by a relationship $\varepsilon = (2a - 1)/3$, ensuing from Flory's theory¹⁷. Appropriate coordinates for representing equation (9) are provided by the system $\log [(\overline{S}_b^2)_z/A]/\log M_w$, against $(1 + \varepsilon)$, since experimental data (which determine the ordinate) obtained in various solvents ought to lie on a straight line with a unit slope. The expression $\log [(\overline{S}_b^2)_z/A]/\log M_w$ for a given solvent should have the same value for all polydisperse polymers, irrespective of molecular weight and the degree of branching. The constant A values (Table III) can be obtained by measuring radii of gyration of linear nonfractionated poly(methyl methacrylates). In spite of the scatter of experimental points, due to a fairly large error in measurements of $(\overline{S}_b^2)_z$, the determined radii of gyration of four branched polymers show (Fig. 3, Table III) that in thermodynamically not too good solvents the sizes of the branched polymers are larger, and in thermodynamically good solvents they are smaller than would correspond to the assumed equality between the expansion coefficients of the linear and the branched polymers. This finding is consistent with the viscometric results.

Determination of the Degree of Branching

From the viewpoint of characterization of polydisperse branched polymers it is important to know what information on the branched polymer may be obtained from viscometric measurements. The degree of branching based on the measured values of $[\eta]_b$ and M_w (or P_w) is easiest to determine from a plot containing dependences for various values of γ in the coordinates $[\eta]$ against P_w (Fig. 4).

The position of the straight lines for a given γ with respect to the straight line for a linear monodisperse polymer is determined by the expression $[\eta]_b = [\eta]_l Q_b$ (Eq. (6)); consequently, it depends also on the value of the exponent b (Table II). Exponent b may be affected by the topology of the branched molecules (Fig. 1a). In thermodynamically good solvents, where the de-

TABLE III

Values of the Refractive Index Increment, dn/dc (in ml g^{-1} , 5461 Å), of the Constant A of Eq. (8) and the Constants K and a of the Mark-Houwink Equation for Various Solvents, 25°C

Solvent	dn/dc	$A \cdot 10^2$	$K \cdot 10^3$	a
1,4-Dioxan-water ^a	0.0965 ^b	10.17	47.40	0.52
Butyl acetate ^c	0.0970	7.76	18.70	0.60
Ethyl acetate	0.1180 ^d	6.30	7.58	0.70
1,4-Dioxan	0.0707	4.82	6.54 ^e	0.75 ^e

^a Concentration of water 17% by vol.. ^b Ref.¹⁵, measured after the establishment of the dialysis equilibrium between the solution and the solvent; ^c ref.¹; ^d ref.¹⁶; ^e ref.¹⁷.

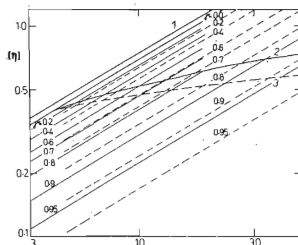
pendence of b on the density of the branching centres is either very weak or none at all (Fig. 3), only one single system of straight lines in a graph of the type shown in Fig. 4 is sufficient for the determination of γ ($b = \text{constant}$ for the given type of the branched polymer).

It follows from the above that an accurate viscometric determination of the degree of branching of polydisperse polymers requires a fairly large number of preliminary measurements on polymers having a similar content of the branching agent and different degrees of branching (determined independently, for instance from P_w and $P_{w,0}$); these measurements will then allow us to determine a suitable value of b for the given system polymer-solvent (by plotting experimental data in the coordinates $[\eta]_b/[\eta]_l$ against $(1 - \gamma)$ and using the graph in Fig. 2, if available).

FIG. 4

A Plot for the Determination of the Degree of Branching, γ , from the Values of $[\eta]_b$ (in dl g^{-1}) and M_w or P_w in the System Poly-(Methyl Methacrylate)-Butyl Acetate

$a = 0.60$. 1 Dependence for a monodisperse linear polymer; $\gamma = 0$ polydisperse linear polymer with the most probable distribution of molecular weights (*i.e.* primary chain); ——— $b = 0.5$, - - - - $b = 0.8$; 2 and 3 dependences for polymers having different degrees of branching derived from the primary chain with $P_{w,0} = 4 \cdot 10^3$ for $b = 0.5$ and 0.8 .



In practice, however, an independent determination of γ is sometimes not feasible. In this case, the degree of branching must be estimated without knowing the correct value of exponent b . Neither in this case, however, will the error of determination of γ within the interval $0.5 < \gamma < 1.0$ exceed that involved in the determination based on the values of P_w and $P_{w,0}$ (Fig. 1a). For $\gamma < 0.5$ the error may be somewhat higher. Thus, for instance, for $P_w = 10^4$ and $[\eta]_b = 0.65$ we shall read for $b = 0.5$ the value $\gamma = 0.2$, whereas for $b = 0.8$ we shall estimate by interpolation $\gamma = 0.15$; for $P_w = 10^4$ and $[\eta]_b = 0.3$, the following pairs of values will be found: $b = 0.5$, $\gamma = 0.9$ and $b = 0.8$, $\gamma = 0.82$. In thermodynamically good solvents the error committed while estimating γ within the given interval is even smaller.

It should be noted that the average number of the branch units in a macromolecule corresponding to the value of γ determined by the procedure outlined above may be calculated by using known relationships^{3,4}. Thus, the z -average of the g -factor for tetrafunctional branch units is related to the weight average number of the branch units in a molecule, n_w , by the expression

$$g_z = 1 - \gamma = 1/(1 + n_w). \quad (10)$$

For the sake of illustration, Fig. 4 represents also the theoretical dependences for $b = 0.5$ and $b = 0.8$, according to which the intrinsic viscosity of the primary linear poly(methyl methacrylate) with $P_{w,0} = 4 \cdot 10^3$ ought to change with proceeding branching. As has been shown¹⁸, the experimental dependences are in a very good agreement with the theoretical ones.

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