

Characterization of Branched Polydisperse Polymers. Influence of Solvents on the Branching Parameters

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Synopsis

The influence of solvents on the branching degrees G (the ratio of intrinsic viscosities) and g (the ratio of radii of gyration), and on the branching exponent b in equation $G = g^b$ has been estimated using the recently reported equations for branched polymers. The following relations have been found: $G < G_0$, $\bar{g}_x = \bar{g}_{x,0}$, and $b > b_0$, where subscripts 0 and x denote the unperturbed (or theta) conditions and the type of average value for polydisperse polymers, respectively. Hence the expansion coefficients of branched and linear macromolecules are related by $\alpha_{\eta,br} < \alpha_{\eta,lin}$ and $\alpha_{s,br} = \alpha_{s,lin}$.

INTRODUCTION

Branched polymers are usually characterized by the following branching degrees¹⁻¹⁰

$$G = [\eta]_{br}/[\eta]_{lin} \quad (1)$$

and

$$g = \langle r^2 \rangle_{br}/\langle r^2 \rangle_{lin} \quad (2a)$$

or

$$g = \langle s^2 \rangle_{br}/\langle s^2 \rangle_{lin} \quad (2b)$$

for the same molecular weight (M) of branched (br) and linear (lin) molecules, where $[\eta]$, $\langle r^2 \rangle$, and $\langle s^2 \rangle$ are the intrinsic viscosity, mean square end-to-end distance and mean square radius of gyration of macromolecules, respectively. The branching degrees G and g are related by

$$G = g^b \quad (3)$$

where b is the branching exponent dependent above all on the type of branching (star, comb, or random). The reported values of b are in the range from 0.5 (the theoretical value of Zimm and Kilb for starlike branching²) to 1.5 (the theoretical value derived with the assumption that the Flory constants for branched and linear macromolecules are equal, $\Phi_{br} = \Phi_{lin}$; cf. Ref. 5).

Since the theoretical considerations are based on the random flight statistics of macromolecule, the unperturbed values should be taken for $[\eta]$, $\langle r^2 \rangle$, or $\langle s^2 \rangle$ in eqs. (1)–(3). Hence, the branching degrees G_0 and g_0 for the unperturbed conditions can be defined as

$$G_0 = [\eta]_{0,br}/[\eta]_{0,lin} \quad (4)$$

and

$$g_0 = \langle r^2 \rangle_{0,br}/\langle r^2 \rangle_{0,lin} \quad (5a)$$

or

$$g_0 = \langle s^2 \rangle_{0,br}/\langle s^2 \rangle_{0,lin} \quad (5b)$$

The theoretical unperturbed conditions for the second virial coefficient $A_2 = 0$ and the experimental theta conditions can be distinguished, as reviewed by Small.⁴ However, we assume that according to the Flory theory we have

$$G_0 = G_{\Theta} \quad (6)$$

and

$$g_0 = g_{\Theta} \quad (7)$$

where subscripts 0 and Θ denote the unperturbed and theta conditions, respectively. In fact, the theta temperatures for linear and randomly branched polymers are very close or identical.⁶

In considerations of influence of solvents on the branching degrees G and g , the expansion coefficients α_{br} and α_{lin} for branched and linear macromolecules in solution should be taken into account. Then we have

$$G = (\alpha_{\eta,br}^3/\alpha_{\eta,lin}^3)G_0 \quad (8)$$

and

$$g = (\alpha_{r,br}^2/\alpha_{r,lin}^2)g_0 \quad (9a)$$

or

$$g = (\alpha_{s,br}^2/\alpha_{s,lin}^2)g_0 \quad (9b)$$

where $\alpha_{\eta}^3 = [\eta]/[\eta]_0$, $\alpha_r^2 = \langle r^2 \rangle/\langle r^2 \rangle_0$, $\alpha_s^2 = \langle s^2 \rangle/\langle s^2 \rangle_0$, and $\alpha_{s,lin} = \alpha_{r,lin}$. A lot of discrepancies exist, if the theoretical and experimental data are compared with eqs. (8) and (9). For example $G > G_0$,¹¹ $G = G_0$,^{6,12–14} or $G < G_0$,^{6,8,11,15–19} have been reported, and $g > g_0$,^{3,7,8,20–22} or $g = g_0$,^{12,23–25} have theoretically or experimentally been found, or have been assumed.

It has also been reported that the exponent b in eq. (3) depends on the solvent, according to the following relation^{1,24,26,27}:

$$b = 2 - a \quad (10)$$

where a is the Mark-Houwink exponent. Hence, it should be $b < b_0$ and $b_0 = 1.5$. Some authors, however, found that $b > b_0$ with b_0 about 0.5–1.0.^{4,8,15,22} Mostly, the constant value of b as independent of the solvent quality has been applied,^{4,5,24,28} which might be supported by some experimental reports, (cf. Ref. 29).

It has recently been suggested¹⁰ that the influence of solvents on the branching parameters can be taken into account using the following general relationship for the average branching degree g :

$$\bar{g}_{x,f} = [(f/2 - 1)\bar{n}_{bx,f} + 1]^k \quad (11)$$

where f is the functionality of branching, \bar{n}_b is the average number of branch points, and x refers to the type of average values ($x = n$ for number and $x = w$ for weight averages). The exponent k in eq. (11) is given by the following relation¹⁰:

$$k = -a/(ba_{ib}) \quad (12)$$

where a is the Mark-Houwink exponent, b is the branching exponent defined by eq. (3), and a_{ib} is the branching exponent in the power dependence of the glass transition temperature T_g on molecular weight, polydispersity, and branching.^{9,10,30}

In the present work the above-mentioned suggestion¹⁰ is considered and the influence of solvents on G , g , and b is discussed.

DISCUSSION

Branching Degree g_v

The new branching degree g_v , based on gel permeation chromatography (GPC) and viscometric (VIS) measurements, has recently been defined^{31,32} as

$$g_v = \bar{M}_{v, \text{GPC}} / \bar{M}_{v, \text{VIS}} \quad (13)$$

where $\bar{M}_{v, \text{GPC}}$ and $\bar{M}_{v, \text{VIS}}$ are the viscosity average molecular weights determined by GPC and VIS, respectively. This branching degree is related to the other branching parameters by the relation^{9,32}

$$G = g_v^{-a} \quad (14)$$

where a is the Mark-Houwink exponent. Moreover, it has been found that the number average number of chain ends per molecule $\bar{\omega}_n$ is related to g_v by

$$\bar{\omega}_n = 2ga_{ib} \quad (15)$$

where a_{tb} is obtained from the T_g measurements.³⁰

It is evident that the average number of chain ends per molecule $\bar{\omega}_n$ is a structural parameter independent of solvent. Since the value of a_{tb} is also independent of solvent, we have from eq. (15) that $g_v = \text{const}$ for different solvents.

Branching Degree G

It results immediately from eq. (14) that the branching degree G depends on the solvent quality, characterized by the Mark-Houwink exponent a . An example for polycarbonate is shown in Table I. It is evident that the highest values of G are obtained for the theta solvent, and $G < G_0$. However, differences between values of G for different solvents are rather small (cf. Table I). This is probably the reason that the experimental values of G , obtained with some errors, are sometimes considered as solvent independent.^{12,13} The results of Orofino and Wenger¹¹ that $G/G_0 = 1.03$ in benzene at 25°C and $G/G_0 = 1.04$ in toluene at 30°C for models of polystyrene are opposed by the same authors by $G/G_0 = 0.97$ in cyclohexane at 40°C.

The relation $G < G_0$ has been confirmed by many other authors.^{6,8,15-19}

Branching Degree g

Combining eqs. (3) and (14), we obtain

$$g = g_v^{-a/b} \quad (16)$$

It has previously been found^{9,10,33} that

$$b = a_m/a_{mbG} \quad (17)$$

where a_m and a_{mbG} are the exponents for M and for branching degree G , respectively, in the power dependence of the zero shear rate melt viscosity η_0 on molecular weight, polydispersity, and branching,^{9,10,33} written as

$$\eta_0 = A_m \bar{M}_x^{a_m} Q^{a_{mpz}} G^{a_{mbG}} \quad (18)$$

TABLE I
Dependence of Branching Degree G on the Solvent Quality

Sample	Branching degree g_v^a	Branching degree G from eq. (14)				
		$a = 0.50$	$a = 0.60$	$a = 0.70$	$a = 0.76$	$a = 0.82$
DE-16	1.02	0.990	0.988	0.986	0.985	0.984
DEM-1	1.06	0.971	0.966	0.960	0.957	0.953
DE-2	1.10	0.953	0.944	0.935	0.930	0.925
DE-4	1.20	0.913	0.896	0.880	0.871	0.861
DE-8	1.25	0.894	0.875	0.855	0.844	0.833
DE-13	1.29	0.880	0.858	0.837	0.824	0.812
DE-7	1.68	0.772	0.733	0.695	0.674	0.654

^a The experimental values of g_v are taken from Ref. 33.

If the branching degree g_v instead of G is applied in eq. (18), the branching exponents are related by

$$a_{mbG} = -a_{mbg_v}/a \quad (19)$$

Then, combining eqs. (17) and (19), we obtain

$$b = -a \cdot a_m/a_{mbg_v} \quad (20)$$

Thus the branching exponent b depends on the solvent through the Mark-Houwink exponent a ; the values of a_m and a_{mbg_v} are solvent-independent. Combining eqs. (16) and (20), we have

$$g = g_v^{ambg_v/am} \quad (21)$$

Since all magnitudes on the right-hand side of eq. (21) are solvent-independent, the branching degree g is also independent of the solvent. Thus

$$g = g_0 \quad (22)$$

is found.

This result contradicts the relations $g > g_0$ or $\alpha_{s,br} > \alpha_{s,lin}$ [cf. eq. (9b)], calculated by Kron and Ptitsyn²⁰ and Berry and Orofino.²¹ It seems that their assumptions made for theoretical calculations performed on model branched structures are not satisfied for the real branched polymers. On the other hand, the theoretical considerations of Fixman²³ have led to the conclusion that branching has little effect on α_s , which implies $\alpha_{s,br} = \alpha_{s,lin}$ and then $g = g_0$.

Moreover, starting from eq. (11) and substituting

$$\bar{n}_{bx,f} = (\bar{\omega}_x - 2)/(f - 2) \quad (23)$$

(cf. Ref. 10), we obtain

$$\bar{g}_x = (\bar{\omega}_x/2)^k \quad (24)$$

independently of functionality of branching f . Then, combining eqs. (12) and (20), we find that

$$k = a_{mbg_v}/a_m \cdot a_{tb} \quad (25)$$

Thus, k is the solvent-independent exponent, and, in turn, \bar{g}_x in eq. (24) is also independent of the solvent, i.e.,

$$\bar{g}_x = \bar{g}_{x0} \quad (26)$$

It means that the branching degree g is independent of the solvent for monodisperse and polydisperse polymers, independently of functionality of branching.

Branching Exponent b

The branching exponent b depends on the solvent quality according to eq. (20), which can be written as

$$b = D \cdot a \quad (27)$$

where the constant $D = -a_m / a_{mbgv}$ is independent of the solvent and can be determined from the zero-shear-rate melt viscosity dependence on molecular weight, polydispersity, and branching¹⁰ [cf. eqs. (17)–(20)]. If the branching exponent b' for a given solvent characterized by the Mark–Houwink exponent a' is known, the values of b for other solvents can easily be found from

$$b = (b'/a')a \quad (28)$$

If the known value is $b' = b_0$ for the unperturbed conditions, we have

$$b = 2b_0a \quad (29)$$

Hence, values of b higher than 1.5 can be predicted, e.g., for polymers with $b_0 = 1.0$ in good solvents of $a = 0.8$.

The dependence of branching exponent b on the solvent quality according to eqs. (27)–(29) is shown in Figure 1 for randomly branched polymers: low density polyethylene (LDPE), polycarbonate (PC), and polystyrene (PS). The experimental results, taken from published papers, are also included. It should, however, be noted that experimental errors about 30% in determinations of b are not unusual.⁴ Nevertheless, it is evident that the experimental data agree with the predicted increase of b with the increase of solvent quality, i.e., $b > b_0$, contrary to the theoretical results from eq. (10).

The most reliable values of b_0 are ranged from 0.5, as Zimm and Kilb found theoretically for star-branched polymers,² to about 1.0 found for comb-like and randomly branched molecules. These limits as a function of solvent quality are shown in Figure 1. The values of b for randomly branched polymers with $b_0 = 0.55$ – 0.60 for PS, $b_0 = 0.75$ – 0.80 for PC and $b_0 = 0.8$ – 1.0 for LDPE lies within these limits.

Therefore, it can be concluded that the number of branch points obtained from the theoretical equations $\bar{g}_w = f(\bar{n}_{bw})$, derived by Zimm and Stockmayer¹ with the assumption that $b_0 = 1.5$ for the unperturbed conditions, cannot agree with experimental results.¹⁰

CONCLUDING REMARKS

It has been found that solvents affect the branching degree G and the branching exponent b , while the branching degree g is independent of the solvent. The following relations have been found: $G < G_0$, $\bar{g}_x = \bar{g}_{x0}$, and $b > b_0$, as well as $\alpha_{\eta,br} < \alpha_{\eta,lin}$ and $\alpha_{s,br} = \alpha_{s,lin}$. Thus it has been found that the solvent effect of branching is more pronounced for α_{η} (hydrodynamic

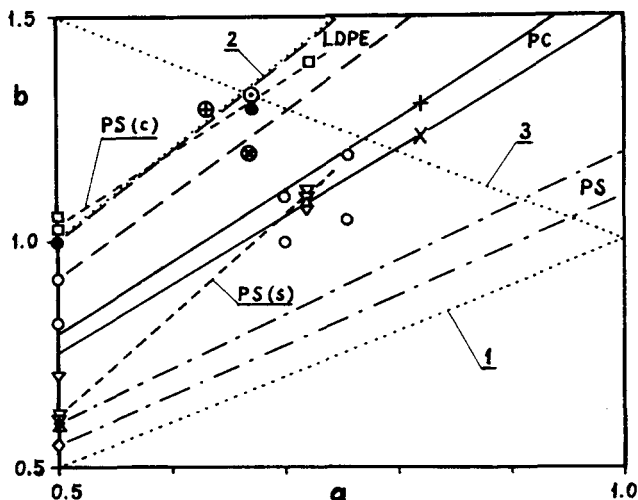


Fig. 1. Dependence of branching exponent b on the solvent quality. (—) LDPE, eq. (29), with $b_0 = 0.92$ (lower line)⁸ and $b_0 = 1.00$ (upper line)^{4,13}; experimental points: (●) Small,⁴ according to Hama et al.¹³; (○) Arndt and Schröder⁸ with the values of a for good solvents given by Wulfert³⁴; (⊗) Casper et al.¹⁴; (⊕) Cote and Shida²⁷; (⊗) Völker and Luig³⁵; (—) PC, eq. (28) with $b' = 1.24$ for $a' = 0.82^{10}$ (×, lower line) and $b' = 1.31$ for $a' = 0.82^{33}$ (+, upper line); (---) randomly branched PS, eq. (29), with $b_0 = 0.55$ (lower line)¹⁰ and $b_0 = 0.60$ (upper line)²⁹; (◆) Kurata et al.²⁹; (◇) Dobkowski,¹⁰ according to the data of Masuda et al.³⁶; (---) model polystyrenes: PS(s) = star-branched: (∇) Meunier and Van Leemput¹⁵; (△) Berry²²; PS(c) = comb-branched: (□) Berry²²; (· · ·) (1) theoretical limit for star-branched polymers, $b_0 = 0.5$, eq. (29); (2) theoretical limit for comb-branched polymers, $b_0 = 1.0$ eq. (29); (3) theoretical values of b according to $b = 2 - a$, eq. (10).

conditions) than that for α_s (static conditions of measurements). It can also be concluded that the ratio α_η/α_s depends on branching and $\alpha_\eta/\alpha_s)_{br} < (\alpha_\eta/\alpha_s)_{lin}$. Hence the ratio of Flory constants should be lower for branched molecules, i.e., $(\phi/\phi_0)_{br} < (\phi/\phi_0)_{lin}$.

All these results, based on empirical relationships, should be checked by further experimental and theoretical works.

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