

Application of Multimethod Procedure for Characterization of Branched Polydisperse Polymers

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Synopsis

The multimethod procedure for characterization of branched polydisperse polymers, including gel permeation chromatography, solution viscometry, melt viscometry, and differential scanning calorimetry, is described. An equation relating the average branching degree \bar{g}_x and the average number of branch points \bar{n}_{bx} has been derived and compared with the theoretical Zimm-Stockmayer equation. It has been found that both equations can be consistent for theta solvent and for the branching degree exponent $b = 1.5$. Experimental data are given for trifunctionally branched bisphenol A polycarbonate.

INTRODUCTION

Since the theoretical work of Zimm and Stockmayer,¹ the influence of long chain branching (LCB) on polymer properties has been considered by many authors, both from theoretical and experimental points of view (for references see reviews and some recent works²⁻⁶). Experimental characteristics of branched polymer should contain the determination of molecular weight (M) or M averages (\bar{M}_x), molecular weight distribution (MWD), and parameters of branched structure such as the type of branching (star, comb, or random), the branch point (or branch unit) functionality f , the number of branch points per molecule n_b , the distribution of branch points, etc. Commonly used branching degrees

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

or

$$g = \overline{r_{\text{br}}^2}/\overline{r_{\text{lin}}^2} \quad (2)$$

where $[\eta]$ is the intrinsic viscosity, $\overline{r^2}$ is the mean square end-to-end distance of macromolecule, and subscripts br and lin denote branched and linear polymers, respectively, give only a very general indication of the amount of branched species. The two branching degrees G and g are related by

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

where the branching degree exponent b depends above all on the type of branching and varies from 0.5 to 1.5 (cf. Refs. 2 and 3). Some characteristics, e.g., type of branching and functionality f , can be deduced from conditions of branching reactions.

Theoretical equations, relating the branching degree g and the number of branch points n_b , were derived by Zimm and Stockmayer¹ for randomly branched monodisperse and polydisperse polymers. Thus for polydisperse polymers and

$f = 3$

$$\bar{g}_{3,w} = \frac{6}{\bar{n}_{bw}} \left\{ \frac{1}{2} \left(\frac{2 + \bar{n}_{bw}}{\bar{n}_{bw}} \right)^{1/2} \ln \left[\frac{(2 + \bar{n}_{bw})^{1/2} + \bar{n}_{bw}^{1/2}}{(2 + \bar{n}_{bw})^{1/2} - \bar{n}_{bw}^{1/2}} \right] - 1 \right\} \quad (4)$$

and for $f = 4$

$$\bar{g}_{4,w} = \frac{1}{\bar{n}_{bw}} \ln(1 + \bar{n}_{bw}) \quad (5)$$

where $\bar{g}_{f,w}$ is the weight average value of g for the branch point functionality f and \bar{n}_{bw} is the weight average number of branch points per molecule. Thus \bar{n}_{bw} values should be known for experimental verification of eqs. (4) and (5).

Recently, the following general equation for polymer properties dependent on their molecular characteristics was proposed⁷:

$$P = A_P \prod_{i=1}^n v_i^{a_{iP}} \quad (6)$$

where P is the polymer property, π is the product symbol, v_i is the i th variable of molecular characteristics, such as M and measures of MWD and LCB, and A_P and a_{iP} are constants. Equation (1) offers a method for experimental characterization of branched polydisperse polymers. For example, the values of number average number of branch points \bar{n}_{bn} can be determined from glass transition temperature measurements.⁸

In the present work (presented in part at the Annual Meeting of Polish Chemical Society, Lublin, September 22–25, 1982) the multimethod procedure, including gel permeation chromatography (GPC), solution viscometry (VIS), melt viscometry, and differential scanning calorimetry (DSC), is described. The results are compared with the theoretical Zimm–Stockmayer equation. Randomly branched bisphenol A polycarbonate (PC) with trifunctional branch points is used as an example.

MULTIMETHOD PROCEDURE

The multimethod procedure is based on the general equation, (6), which is applied for selected polymer properties dependent on M , MWD, and LCB. Several samples of branched polydisperse polymer are characterized by GPC and VIS methods. Thus the averages of M , \bar{M}_n , \bar{M}_w , $\bar{M}_{v,GPC}$ and $\bar{M}_{v,VIS}$ are obtained. The polydispersity degree

$$q = \bar{M}_w / \bar{M}_n \quad (7)$$

and the branching degree

$$g_v = \bar{M}_{v,GPC} / \bar{M}_{v,VIS} \quad (8)$$

are used as measures of MWD and LCB, respectively.^{7–12} The branching degree g_v is related to the other branching degrees by the following equation^{7,10}:

$$G = g_v^{-a_s} \quad (9)$$

where a_s is the exponent of the Mark–Houwink equation

$$[\eta] = KM^{a_s} \quad (10)$$

The GPC system should be properly calibrated in order to obtain $g_v = 1$ for linear and $g_v > 1$ for branched polymers.

Polymer properties, measured and then treated according to eq. (6) to obtain constants A_P and a_{iP} by the least-squares four-variable regression method, are specified below.

1. Intrinsic viscosity $[\eta]$ for checking the reliability of molecular characteristics^{7,9-11}:

$$[\eta] = A_s \bar{M}_x^{a_s} q^{a_{spx}} g_v^{a_{sb}} \quad (11)$$

where indices s , x , p , and b denote the intrinsic viscosity as the polymer solution property, the type of M average, polydispersity, and branching, respectively. The branching degree G can be used in eq. (11) instead of g_v , and then

$$[\eta] = A_s \bar{M}_x^{a_s} q^{a_{spx}} G^{a_{sb}} \quad (11a)$$

where the branching exponent $a_{sb} = 1$ for G .

If GPC and VIS measurements of M , MWD, and LCB are correct, the constants of the Mark-Houwink equation $K = A_s$ and a_s for a given polymer-solvent system should be obtained by the least-squares method. Moreover, the following conditions should be satisfied⁷:

$$a_{spn} > 0 \quad (12a)$$

$$a_{spv} = 0 \quad (12b)$$

$$a_{spw} \leq 0 \quad (12c)$$

for the polydispersity exponent a_{spx} , and

$$a_{sb} = -a_s \quad \text{for } g_v \quad (13a)$$

or

$$a_{sb} = 1 \quad \text{for } G \quad (13b)$$

Then the other polymer properties can be measured.

2. Zero shear rate melt viscosity η_0 as the melt property^{7,12}:

$$\eta_0 = A_m \bar{M}_x^{a_m} q^{a_{mpx}} G^{a_{mb}} \quad (14)$$

where subscript m denotes the melt property and G is used as the measure of LCB. Then the exponent b of eq. (3) can be obtained from eq. (14) as the following ratio⁷:

$$b = a_m / a_{mb} \quad (15)$$

3. Glass transition temperature T_g and $\Delta T_g = T_{g0,\infty} - T_{g0}$, where $T_{g\infty}$ is the value of T_g at $M = \infty$, and the subscript 0 denotes T_g values at zero heating rate, treated by the following general equation:

$$\Delta T_g = A_t (\bar{M}_x + B q^{a_{tpx}} g_v^{a_{tb}})^{a_t} q^{a_{tpx}} g_v^{a_{tb}} \quad (16)$$

where the subscript t denotes ΔT_g as the polymer property, B is the correction for M , and $a_t = -1$.^{7,8} Thus, the number average number of chain ends per macromolecule $\bar{\omega}_n$ can be calculated⁸:

$$\bar{\omega}_n = 2g_v^{a_{tb}} \quad (17)$$

Hence, the other LCB parameters are found, i.e., the number average number of branch points per molecule \bar{n}_{bn} , the average \bar{M}_n of segments between branch points $\bar{M}_{n,seg}$, and the average number of branch points per average M (the branching frequency) λ_n , according to the following relations:

$$\bar{n}_{bx,f} = (\bar{\omega}_x - 2)/(f - 2) \quad (18)$$

$$\bar{M}_{x,seg} = \bar{M}_x / \left[\frac{f-1}{f-2} (\bar{\omega}_x - 2) + 1 \right] \quad (19)$$

$$\lambda_x = \bar{n}_{bx} / \bar{M}_x \quad (20)$$

Thus, for $f = 3$ we have⁸

$$\bar{n}_{bn,3} = \bar{\omega}_n - 2 \quad (18a)$$

$$\bar{M}_{n,seg} = \bar{M}_n / (2\bar{n}_{bn,3} + 1) \quad (19a)$$

and for $f = 4$

$$\bar{n}_{bn,4} = (\bar{\omega}_n/2) - 1 \quad (18b)$$

$$\bar{M}_{n,seg} = \bar{M}_n / (3\bar{n}_{bn,4} + 1) \quad (19b)$$

Therefore, combining eqs. (3), (9), (17), and (18), we obtain

$$\bar{g}_{f,n} = [(1/2f - 1)\bar{n}_{bn,f} + 1]^k \quad (21)$$

where $\bar{g}_{f,n}$ is the number average value of g for the branch points functionality f , and

$$k = -a_s/ba_{tb} \quad (22)$$

and $b = a_m/a_{mb}$ according to eq. (15). Hence, for $f = 3$ we have

$$\bar{g}_{3,n} = (1/2\bar{n}_{bn,3} + 1)^k \quad (23a)$$

and for $f = 4$

$$\bar{g}_{4,n} = (\bar{n}_{bn,4} + 1)^k \quad (23b)$$

Combining eqs. (18) and (21), we obtain

$$\bar{g}_n = (1/2\bar{\omega}_n)^k \quad (24)$$

independently of branch points functionality f , and introducing eq. (17) into eq. (24), we have

$$\bar{g}_n = g_v^{-a_s/b} \quad (25)$$

Therefore, the essential parameter for determination of branching degree g is the number of chain ends per molecule $\bar{\omega}$, irrespective of branch points functionality f . Values of $\bar{\omega}_n$ are obtained experimentally from T_g measurements,⁸ and eqs.(21)–(23) can be compared with the theoretical Zimm–Stockmayer equations (4) and (5).

EXPERIMENTAL

Samples of randomly branched polydisperse bisphenol A polycarbonate (PC) were laboratory prepared by interfacial polycondensation, using 2,4-bis(p -

hydroxycumyl)phenol (BPX) and phloroglucinol (THB) as trifunctional branching agents.¹⁰ Commercial PC samples of Lexan (General Electric Co.), Makrolon (Bayer AG), and Bistan (Zachem, Poland), some of them supposed to be branched, were used for comparison.

PC samples were characterized by GPC and VIS methods^{7,10} and their $[\eta]$, η_0 , and T_{g0} were measured.^{8,10,12} The following constants were found: $a_s = 0.82$,^{7,9-11} $b = 1.31$,¹² and $a_{tb} = 0.51$.⁸ Hence, the exponent k [eq. (22)] is equal to -1.23 .

RESULTS AND DISCUSSION

Results of molecular characteristics of PC samples are given in Table I. The results were checked by eq. (11a), using the measured values of $[\eta]$, not included in Table I. The following coefficients were obtained: $A_s = 1.31 \times 10^{-2} \text{ cm}^3/\text{g}$, $a_s = 0.812$, $a_{spn} = 0.756$, $a_{spw} = -0.037$, and $a_{sb} = 1.05$ for G . The values of A_s and a_s agree with the Mark-Houwink constants $K = 1.20 \times 10^{-2} \text{ cm}^3/\text{g}$ and $a_s = 0.820$ for PC in CHCl_3 .^{7,10} The conditions of reliability, eqs. (12a), (12c), and (13b), are also satisfied. Nevertheless, the values of G were corrected⁷; however, only small differences between uncorrected and corrected values are observed for higher branch contents (i.e., for lower G values) (see Table I). Then the values of \bar{g}_n and \bar{n}_{bn} for $f = 3$ (the subscript 3 is omitted) were calculated (see Table I) and statistically treated according to eq. (23a). Hence, $k = -1.30$ with correlation coefficient $r^2 = 0.997$ was obtained. This value of k is by 5.7% lower than that calculated from eq. (22). Hence $b = 1.24$. The calculated curve $\bar{g}_n = f(\bar{n}_{bn})$ and the experimental points are shown in Figure 1. Thus, the experimental points for all samples, irrespective of the method of preparation and the type of branching agent, belong to the same curve.

The experimental curve for PC is also compared with the theoretical one of Zimm and Stockmayer given by eq. (4) (see Fig. 1). The difference is evident, and we have found it necessary to consider some simple models in order to comment on such a discrepancy.

Therefore, hypothetical PC samples composed of three to six fractions of branched macromolecules with a given number of branch points n_{bi} were used for calculations of branching parameters. Values of \bar{n}_{bn} and \bar{n}_{bw} were obtained from

$$\bar{n}_{bn} = \sum x_{ni} n_{bi} \quad (26a)$$

and

$$\bar{n}_{bw} = \sum x_{wi} n_{bi} \quad (26b)$$

where n_{bi} is the number of branch points per i th molecule, x_{ni} and x_{wi} are the number and weight fractions, respectively, of the i th molecules. Values of g_i for the i th fractions were calculated from the number of chain ends $\bar{\omega}$, using eq. (24) with $k = -1.30$, and then the number and weight averages of g were obtained from

$$\bar{g}_n = \sum x_{ni} g_i \quad (27a)$$

and

$$\bar{g}_w = \sum x_{wi} g_i \quad (27b)$$

TABLE I
 Characteristics of Branched Polydisperse PC Samples

Type	Samples Branching agent	Symbol	GPC/VIS measurements				Branching degree \bar{g}_v	Branching degree \bar{g}_n^c	Number average number of branch points \bar{n}_{bn}^d
			$\bar{M}_n \times 10^{-3}$ (g/mol)	Average M $\bar{M}_w \times 10^{-3}$ (g/mol)	Polydis- persity degree $q = \bar{M}_w/\bar{M}_n$	Branching degree \bar{g}_v			
Laboratory	BPX	DE-2	13.3	42.5	3.2	1.10	0.92	0.94	0.10
		DE-3	12.7	42.2	3.3	1.23	0.84	0.87	0.22
		DE-4	12.8	47.1	3.7	1.20	0.86	0.88	0.19
		DE-5	13.7	40.5	3.0	1.07	0.95	0.95	0.07
	THB	DE-7	12.2	63.7	5.3	1.68	0.65	0.71	0.61
		DE-8	15.2	59.3	3.9	1.25	0.83	0.82	0.24
		DE-12	13.2	31.9	2.4	1.12	0.91	0.93	0.12
		DE-13	16.5	52.7	3.2	1.29	0.81	0.80	0.28
Commercial	Supposedly BPX	DE-15	24.8	57.8	2.3	1.09	0.93	0.95	0.09
		DE-16	16.2	48.1	3.0	1.02	0.98	0.98	0.02
		DE-17	21.3	52.1	2.4	1.08	0.94	0.94	0.08
		DE-M	19.8	43.5	2.2	1.06	0.95	0.95	0.06
		Bistan AW 3/76	8.6	43.7	5.1	1.20	0.86	0.85	0.19
		AE 23/76 AF	25.4	55.4	2.2	1.08	0.94	0.94	0.08
Not known		MI0	28.5	76.9	2.7	1.16	0.89	0.91	0.16
		RT 499	12.1	33.9	2.8	1.06	0.95	0.96	0.06
		Lexan 151 134	12.6	28.3	2.2	1.00	1.0	1.0	0
		Makrofol E	9.8	42.8	4.4	1.10	0.92	0.92	0.10
		Makrofol 2405	14.1	38.0	2.7	0.99	1.0	1.0	0
		13.6	50.5	3.7	1.22	0.85	0.88	0.21	
		10.1	25.9	2.6	0.99	1.0	1.00	0	

^a From eq. (9) with $a_s = 0.82$.

^b According to eq. (11a); cf. Ref. 7.

^c From eq. (3) with $b = 1.31$.

^d From \bar{g}_v using eqs. (17) and (18a).

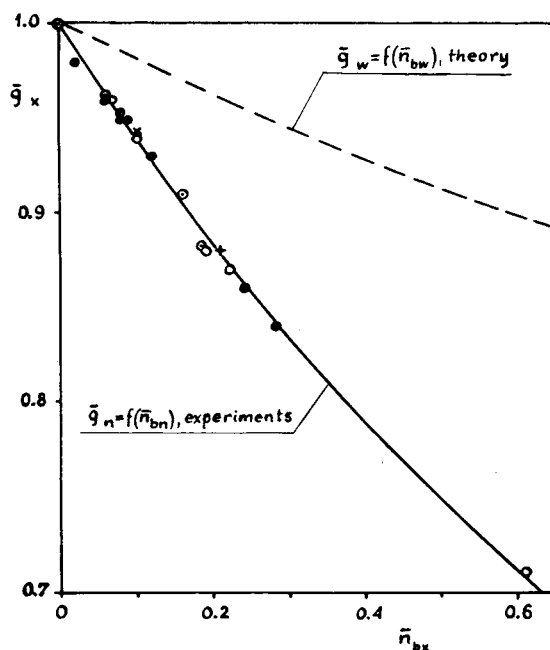


Fig. 1. Average branching degree \bar{g}_x vs. average number of branch points \bar{n}_{bx} . Laboratory PC samples: (O) BPX-branched; (●) THB-branched. Commercial PC samples: (⊙) Bistan; (×) Lexan; (+) Makrolon. (—) Experimental data on PC in chloroform at 25°C, $\bar{g}_n = f(\bar{n}_{bn})$; (---) the theoretical Zimm–Stockmayer equation, $\bar{g}_w = f(\bar{n}_{bw})$, for $f = 3$.

The results of preliminary calculations are shown in Table II and in Figure 2. It is evident that the points for $\bar{g}_n = f(\bar{n}_{bn})$ and for $\bar{g}_w = f(\bar{n}_{bw})$ are placed along the same common curve. It means that both relationships for \bar{g}_n and for \bar{g}_w should be of the same mathematical form and can be written as $\bar{g}_x = f(\bar{n}_{bx})$. Therefore, according to eq. (21), we obtain the following generalized form of $\bar{g}_x - \bar{n}_{bx}$ relationship

$$\bar{g}_{f,x} = [(1/2f - 1)\bar{n}_{bx,f} + 1]^k \quad (28)$$

Hence, for $f = 3$ we have

$$\bar{g}_{3,x} = (1/2\bar{n}_{bx,3} + 1)^k \quad (29)$$

Then the following regression equation was considered:

$$\bar{g}_x = C(1/2\bar{n}_{bx} + 1)^k \quad (30)$$

where the constant C should be equal to unity. The results of calculations for both \bar{g}_n and \bar{g}_w functions are: $C = 1.07$ and $k = -1.30$ with $r^2 = 0.972$. Samples with a quasi-log-normal MWD (see Table II) are even better correlated: $C = 1.04$ and $k = -1.27$ with $r^2 = 0.995$ for both \bar{g}_n and \bar{g}_w functions. Curves of different k values can, however, be distinguished (see Fig. 2). Then it can be suggested that the theoretical Zimm–Stockmayer relation [eq. (4)] is approximated by eq. (29) with k between -0.45 and -0.40 (see Fig. 2). It corresponds to $a_s = 0.5$ (theta solvent), $b = 1.5$ (the theoretical value of Flory; cf. Refs. 2 and 3), and

TABLE II
Preliminary Simple Model Calculations of Branching Parameters

Distributions (assumed)		Branching parameters for $f = 3$						
Type of MWD $x_{wi} = f(M_i)$	Type of branch points distribution $x_{wi} = f(n_{bi})$	Type of n_{bi} vs. M_i relation ^a	\bar{n}_{bn}	\bar{n}_{bw}	[eq. (24)] $\bar{g}_n = \sum x_{ni} \beta_i$	$\bar{g}_w = \sum x_{wi} \beta_i$	\bar{g}_w / \bar{g}_n	
Increasing	Decreasing	h	0.25	0.35	0.86	0.90	0.86	0.96
		m		0.26			0.89	0.99
		m		0.21			0.91	1.01
		l		0.18			0.93	1.03
		h	0.33	0.43	0.82	0.86	0.83	0.97
		m		0.32			0.88	1.02
		l		0.26			0.90	1.05
		h	0.66	0.86	0.69	0.79	0.76	0.96
		m		0.64			0.82	1.04
		l		0.52			0.86	1.09
Quasi-log-normal	increasing monodisperse	increasing constant	1.50	2.43	0.48	0.55	0.37	0.67
		decreasing	1	1	0.59	0.59	0.59	1.00
		decreasing	2	2	0.41	0.41	0.41	1.00
		decreasing	1.50	0.57	0.48	0.55	0.79	1.44
		decreasing	0.06	0.21	0.96	0.98	0.91	0.93
		quasinormal	0.34	0.11	0.82	0.86	0.95	1.10
		quasinormal	0.39	0.70	0.79	0.84	0.72	0.86
		quasinormal	0.73	1.35	0.67	0.73	0.55	0.75
		quasinormal	1.32	1.69	0.52	0.55	0.47	0.85
		quasinormal	1.68	1.31	0.45	0.47	0.54	1.15

^a h, m, or l indicate that high, medium, or low molecular weight fractions are branched, respectively.

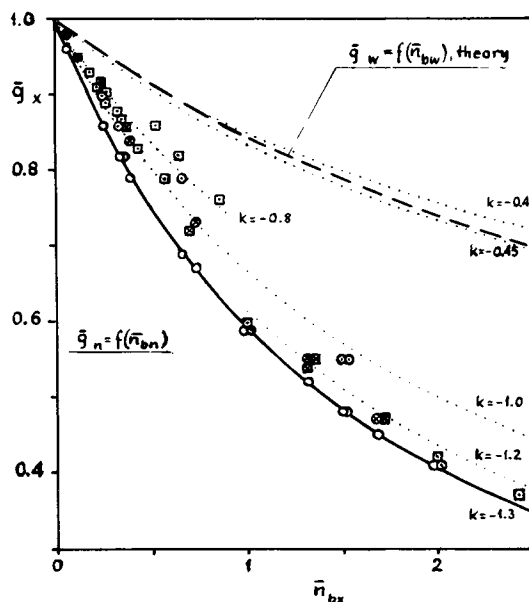


Fig. 2. Average branching degree \bar{g}_x vs. average number of branch points \bar{n}_{bx} from model calculations: (O) $\bar{g}_n = (\bar{\omega}/2)^k$ with $k = -1.30$; (⊙, ⊗) $\bar{g}_n = \sum x_{ni}g_i$; (□, ⊠) $\bar{g}_w = \sum x_{wi}g_i$. Pointed in and crossed data are for increasing and quasi-log-normal molecular weight distributions, respectively.

$a_{tb} \approx 0.8$. In fact, the unperturbed macromolecule coil (i.e., theta conditions) and the statistics of Flory (which gives $G = g^{1.5} \Phi_{br}/\Phi_{lin}$, where Φ is the universal constant) were assumed by Zimm and Stockmayer.¹ Therefore, the influence of solvent is responsible for the observed difference between eqs. (4) and (23a) in Figure 1.

For distinguishing between \bar{g}_n and \bar{g}_w functions given by eq. (28), the ratios \bar{g}_w/\bar{g}_n or $\bar{n}_{bw}/\bar{n}_{bn}$ should be known. It may be expected that the both ratios depend not only on the MWD, i.e., $x_{wi} = f(M_i)$, but also on the branch points distribution, i.e., $x_{wi} = f(n_{bi})$, and above all on the relation $n_{bi} = f(M_i)$. Thus the ratios \bar{g}_w/\bar{g}_n and $\bar{n}_{bw}/\bar{n}_{bn}$ are equal to unity for monodisperse branch points, i.e., for $n_{bi} = \text{const}$, or they are near unity for samples with branched molecules of medium M . If the branch points are connected with molecules of high M , the ratio \bar{g}_w/\bar{g}_n is lower, and the ratio $\bar{n}_{bw}/\bar{n}_{bn}$ is higher than unity; and vice versa, \bar{g}_w/\bar{g}_n is higher and $\bar{n}_{bw}/\bar{n}_{bn}$ is lower than unity for branched low- M species (Table II). These results, based on simple model calculations, seem to be reasonable; they should, however, be confirmed by more complex model calculations and/or by other experimental data, especially on weight average branching parameters. Fortunately, experimental data on randomly branched polystyrene (PS) have quite recently been reported.¹³ We have treated these data according to the multimethod procedure, and the results consistent with those from simple model calculations have been obtained (see the Appendix).

Similarly, the weight average branching parameters can be calculated for PC samples, using equations derived in the Appendix (see Table III). Thus, the ratio $\bar{n}_{bw}/\bar{n}_{bn}$ higher than unity and the ratio \bar{g}_w/\bar{g}_n lower than unity are obtained, i.e., the relation of n_{bi} vs. M_i is an increasing function for all PC samples.

The branching frequencies λ_w and λ_n are shown in Table III and in Figure 3,

TABLE III
 Weight Average branching Parameters of PC Samples

Sample	$\bar{M}_{seg} \times 10^{-3}$	\bar{n}_{bw}^a	$\bar{n}_{bw}/\bar{n}_{bn}$	\bar{g}_w^b	\bar{g}_w/\bar{g}_n	$\lambda_w \times 10^{-6c}$
DE-2	11.1	1.43	14.3	0.50	0.53	33.6
DE-3	8.8	1.87	8.5	0.42	0.48	44.3
DE-4	9.3	2.07	10.9	0.40	0.45	43.9
DE-5	12.0	1.20	17.1	0.54	0.56	29.6
DE-7	5.5	5.39	5.3	0.18	0.25	84.6
DE-8	10.3	2.40	10.0	0.36	0.42	40.5
DE-12	10.6	0.97	8.1	0.60	0.65	30.4
DE-13	10.6	2.00	7.1	0.41	0.49	38.0
DE-15	21.0	0.85	9.4	0.63	0.66	14.7
DE-17	18.4	0.90	11.3	0.62	0.65	17.3
DE-M	17.7	0.74	12.3	0.66	0.69	17.0
Bistan						
AW 3/76	6.2	2.98	15.7	0.31	0.35	68.2
AE 23/76	21.9	0.78	9.8	0.65	0.68	14.1
AF	21.6	1.28	8.0	0.53	0.58	16.6
M-10	10.8	1.07	17.8	0.57	0.59	31.6
Lexan 151	8.2	2.18	21.8	0.38	0.40	50.9
Makrofol E	9.6	2.14	10.2	0.39	0.44	42.4

^a From eq. (36), equivalent results are obtained from eq. (37).

^b From eq. (29) with $k = -1.30$.

^c From eq. (30).

respectively. Both relations given by eqs. (38) and (39) in the Appendix are found to be satisfied. Neglecting a different origin of branched PC samples, $A_n = 5 \times 10^{-7}$ and $a_{2n} = 2.50$ are obtained from eq. (39) with correlation coefficient $r^2 = 0.77$. The exponent a_{2n} calculated from eqs. (38) and (41) is equal to 2.78. The results for BPX-branched laboratory and commercial PC samples are better correlated: $A_n = 3 \times 10^{-7}$ and $a_{2n} = 2.90$ with correlation coefficient $r^2 = 0.87$ are calculated from eq. (39) and $a_{2n} = 2.93$ from eqs. (38) and (41).

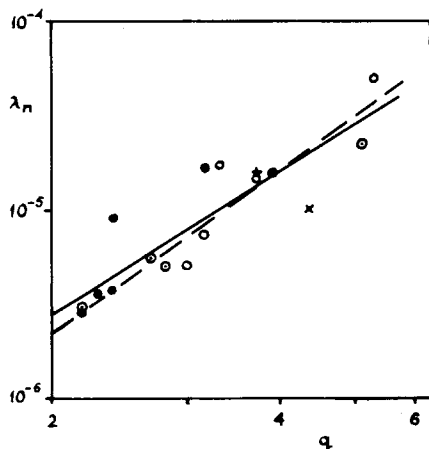


Fig. 3. Branching frequency λ_n vs. polydispersity degree q . Laboratory PC samples: (○) BPX-branched; (●) THB-branched. Commercial PC samples: (○) Bistan; (×) Lexan; (+) Makrofol. (—) All PC samples with correlation coefficient $r^2 = 0.77$; (---) BPX-branched PC samples with correlation coefficient $r^2 = 0.87$.

CONCLUSIONS

The multimethod procedure, based on GPC, VIS, melt viscometry, and DSC methods, enables the improved characterization of branched polydisperse polymers. It is suggested that the relationship, derived for $\bar{g}_n = f(\bar{n}_{bn})$ [eq. (21)] and checked for trifunctionally branched PC, is valid also for $\bar{g}_w = f(\bar{n}_{bw})$, and can be generalized as $\bar{g}_x = f(\bar{n}_{bx})$ [eq. (28)].

Comparison of results on PC and the theoretical equation for $f = 3$ suggests that the influence of solvents on the measurement of the branching degree g should be taken into account by means of eq. (28). Thus, eq. (28) and the theoretical Zimm–Stockmayer relation for $f = 3$ [eq. (4)] are in agreement, if $a_s = 0.5$ (theta solvent) and $b = 1.5$ (the theoretical value of Flory) with a_{tb} about 0.8 for trifunctionally branched PC samples.

The multimethod procedure has been used for branched polydisperse PC; it can, however, be applied for any other polymer. It has been proved for randomly tetrafunctionally branched PS (see the Appendix). Thus, eq. (28) and the theoretical Zimm–Stockmayer relation for $f = 4$, eq. (5), are in agreement, if $a_s = 0.5$ (theta solvent) and $b = 1.5$ (the theoretical value of Flory) with $a_{tb} \approx 0.6$ for tetrafunctionally branched PS samples.

The branching exponent b [eq. (3)] obtained from experimental data is 1.24 and 0.55 for randomly branched PC in chloroform at 25°C and PS in cyclohexane at 34.5°C, respectively.

APPENDIX: APPLICATION OF MULTIMETHOD PROCEDURE FOR CHARACTERIZATION OF BRANCHED POLYDISPERSE POLYSTYRENE

The described multimethod procedure can be applied to randomly branched polydisperse polystyrene (PS), and the recently published results of Masuda et al.¹³ are used for this purpose. Their three PS samples were tetrafunctionally branched with divinylbenzene and then were fractionated. Thus 21 fractions of narrow MWD were characterized by the average molecular weights \bar{M}_n and \bar{M}_w , the intrinsic viscosity $[\eta]$ in cyclohexane at 34.5°C, the molecular weight between branch points \bar{M}_{seg} , and the ratio \bar{M}_w/\bar{M}_{seg} . The values of \bar{M}_{seg} were estimated for the unfractionated samples from the kinetics of copolymerization and considered as constant for thereafter obtained fractions.¹³ However, this last assumption seems to be disputable.

Taking the experimental data of Masuda et al.¹³ into account, the other parameters of molecular characteristics have been calculated (Table IV). They are listed below.

1. The polydispersity degree $q = \bar{M}_w/\bar{M}_n$. For all samples we have $1 \leq q < 1.64$.
2. The branching degree G from eq. (11a) written as

$$G = [\eta]_{br}/A_s \bar{M}_x^{a_s} q^{a_{spx}} \quad (31)$$

where G is defined by eq. (1), $A_s = 7.90 \times 10^{-2} \text{ cm}^3/\text{g}$ and $a_s = 0.5$ (theta solvent) for linear PS in cyclohexane at 34°C.^{7,14} It is assumed that the MWD of considered PS samples can be approximated by the log-normal MWD, since the values of q are below 2.⁷ Hence $a_{spn} = 0.375$ and $a_{spw} = -0.125$. Thus it is observed that samples considered by Masuda et al.¹³ as linear are in fact branched (see Table IV). Only RB 17410 can be considered as linear.

3. The branching degree g_v from eq. (9) with $a_s = 0.5$.

4. The number average number of chain ends $\bar{\omega}_n$ from eq. (19) for $f = 4$. Having the values of $\bar{\omega}_n$, the exponent a_{tb} is obtained from eq. (17). The correlation of $\bar{\omega}_n$ vs. g_v for all samples is not strong ($r^2 = 0.87$), and the constant term is 1.6 instead of 2. However, for 12 PS samples (denoted by ^b in Table IV), $a_{tb} = 1.19$ is obtained with $r^2 = 0.99$ and the constant term equal to 1.8, i.e., only by 10% lower than 2 [cf. eq. (17)]. The values of $\bar{\omega}_n$ are corrected using g_v and $a_{tb} = 1.19$ [eq. (17)]. Then, the number average number of branch points per molecule \bar{n}_{bn} is calculated (results are not included in to Table IV), as well as corrected values of $\bar{M}_{n,seg}$ from eq. (19) (see Table IV). It seems

TABLE IV
Characteristics of Branched Polydisperse PS Samples

Sample	$\bar{M}_w \times 10^{-3}$	$q = \bar{M}_w/\bar{M}_n$	G	g_b	Calculations			$\bar{M}_{seg} \times 10^{-3}$	$\bar{n}_{bw}/\bar{n}_{bn}$	\bar{g}_w/\bar{g}_n
					Primary	ω_n	Corrected			
RB46							46 ^a			
RB464	1120	1.42	0.476	4.414	12.78		50.75	1.45	0.79	
465	762	1.17	0.511	3.830	10.74		50.68	1.19	0.90	
466	489	1.27	0.580	2.973	6.91 ^b		42.94	1.30	0.86	
467	244	1.29	0.704	2.018	4.07 ^b		38.45	1.37	0.87	
468	167	1.27	0.783	1.631	3.23 ^b		38.87	1.39	0.88	
469	100	1.35	0.860	1.352	2.41 ^b		32.40	1.62	0.88	
4610	70.2	1.10	0.923	1.174	2.26 ^b		39.26	1.25	0.97	
RB93							92.8 ^a			
RB934	495	1.50	0.634	2.488	3.71		47.97	1.58	0.78	
935	307	1.33	0.687	2.119	2.99		43.30	1.40	0.85	
936	204	1.50	0.761	1.727	2.31		36.32	1.68	0.81	
937	124	1.45	0.790	1.602	2		26.40	1.64	0.83	
938	76.9	1.44	0.885	1.277	2		26.39	1.88	0.86	
939	61.0	1.45	0.838	1.424	2		16.31	1.74	0.84	
9310	37.0	1.64	0.805	1.543	2		7.47	1.95	0.78	
RB174							174 ^a			
RB1744	566	1.36	0.813	1.513	2.92 ^b		143.2	1.55	0.86	
1745	436	1.33	0.849	1.387	2.59 ^b		134.8	1.57	0.88	
1746	287	1.33	0.913	1.200	2.16 ^b		125.6	1.78	0.90	
1747	191	1	0.929	1.159	2.07 ^b		122.3	1	1	
1748	162	1.17	0.963	1.078	2 ^b		107.4	1.78	0.95	
1749	122	1.28	0.973	1.056	2 ^b		79.5	2.74	0.93	
17410	74.5	1.12	0.982	1.037	2 ^b		58.9	1.96	0.97	

^a The value of Masuda et al.¹³ for unfractionated sample.

^b The results used for calculation of $a_{1b} = 1.19$ with correlation coefficient $r^2 = 0.99$.

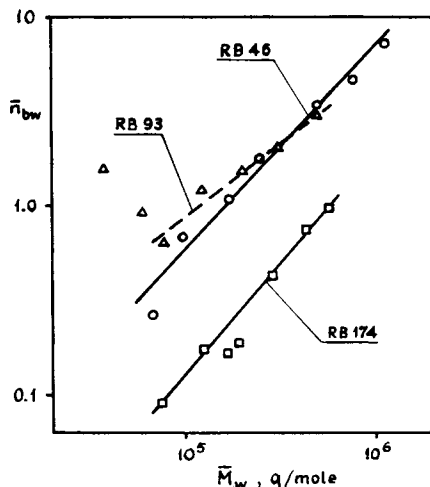


Fig. 4. Weight average number of branch points \bar{n}_{bw} vs. weight average molecular weight \bar{M}_w . Randomly branched PS samples of Masuda et al.¹³: (O) RB 46; (Δ) RB 93; (\square) RB 174.

to be reasonable that \bar{M}_{seg} for unfractionated sample is differentiated in polymer fractions. It is also seen that the authors' value of \bar{M}_{seg} for unfractionated RB93 sample¹³ seems to be overestimated.

Then, taking $\bar{M}_{n,seg} = \bar{M}_{w,seg}$ (it is valid for statistically equal segments and can easily be proved), the weight average number of branch points per molecule \bar{n}_{bw} is calculated via eqs. (18) and (19) for $f = 4$. The dependence of \bar{n}_{bw} on \bar{M}_w , shown in Fig. 4, is approximately linear in logarithmic coordinates for primary RB46, RB93, and RB174 samples, respectively. Thus we have

$$\bar{n}_{bw} = A\bar{M}_w^{a_1} \quad (32)$$

Equations (32) and (20) are identical, if $a_1 = 1$ and $A = \lambda$. It is suggested that both equations are valid for monodisperse samples, while for polydisperse samples the relation of \bar{n}_{bw} vs. \bar{M}_w depends on MWD. Hence

$$\bar{n}_{bw} = A\bar{M}_w^{a_1} q^{a_2} \quad (33)$$

Coefficients of regression equations for primary PS samples are shown in Table V. Therefore, we have $A = \lambda$ as the constant value for monodisperse species, $a_1 = 1$ and $a_2 = 1.7$ for each sample, excluding RB93 (e.g., experimental errors in determination of $[\eta]$ or disturbances in conditions of branching reactions should be considered for RB93 sample).

5. The number average branching degree \bar{g}_n from eq. (3) or from eqs. (21) or (28), as well as the weight average branching degree \bar{g}_w from eq. (28). The exponent b is obtained from eq. (14) applied for polymer solution.⁷ Values of η_0 of 50% PS solution in chlorinated diphenyl KC-5 at 50°C are taken from Figure 4 in Ref. 13. The concentration term is constant, as well as the temperature factor, and both are included in the constant A_m [eq. (14)]. Hence $b = 0.55$ and then $k = -0.76$ are obtained. The value of $b = 0.55$ agrees with $b = 0.6$ reported earlier by Kurata et al.¹⁵ for randomly branched PS.

6. The ratios of $\bar{n}_{bw}/\bar{n}_{bn}$ and \bar{g}_w/\bar{g}_n (Table IV). For all PS fractions of narrow MWD, $\bar{n}_{bw}/\bar{n}_{bn} > 1$ and $\bar{g}_w/\bar{g}_n < 1$ are observed. It means that n_{bi} vs. M_i is an increasing function for each fraction.

7. The branching frequency λ_x from eq. (20). The branching frequency λ_w of fractions vs. \bar{M}_w is not constant (see Fig. 5). It is increasing or decreasing due to differences in MWD and branch points distributions. Similar influence has recently been illustrated for polyethylene¹⁶ and for copolymers,¹⁷ and it is not an unexpected result as some authors consider.¹⁷ If we compare eqs. (20) and (33), we obtain

$$\lambda_w = Aq^{a_2} \quad (34)$$

TABLE V
Coefficients of Regression Equations for $\bar{n}_{bu} = f(\bar{M}_w)$

Type of relationship	Coefficients	RB 46	RB 93	RB 174
Two-variable, eq. (2)	$A \times 10^6$	1.92	95.6	0.18
	a_1	1.09	0.79	1.17
	Correlation r^2	0.968	0.969	0.997
Three-variable, eq. (33)	Number of data	7	5	5
	$A \times 10^6$	2.55	79.6	0.51
	a_1	1.04	0.79	1.05
	a_2	1.74	0.50	1.69
Two-variable, eq. (34)	Correlation r^2	0.982	0.971	0.991
	Number of data	7	5	7
	$A \times 10^6$	3.94	6.37	0.92
	a_2	1.92	0.49	1.89
	Correlation r^2	0.51	0.02	0.85
	Number of data	7	5	7

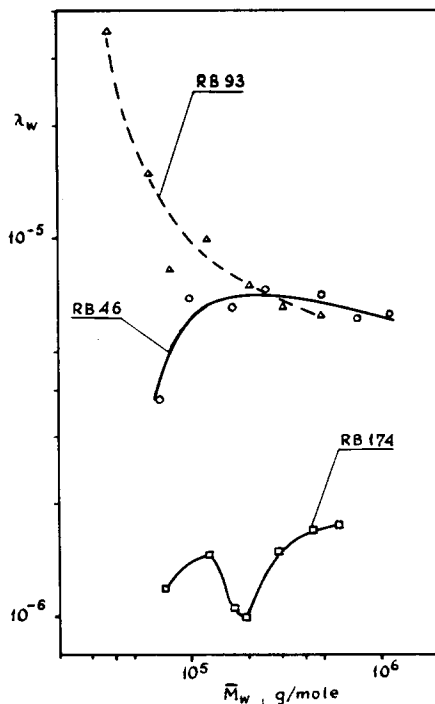


Fig. 5. Branching frequency λ_w vs. weight average molecular weight \bar{M}_w . Symbols are as in Figure 4.

The experimental results of Masuda et al.¹³ are consistent with eq. (34) (see Fig. 6 and Table V).

The relation (28) for $f = 4$ is compared with the theoretical one of Zimm and Stockmayer,¹ eq. (5) (see Fig. 7). Again it is evident that both equations can be represented by similar curves, if $k \approx -0.55$, i.e., for $a_s = 0.5$ (theta solvent), $b = 1.5$ (the theoretical value of Flory), and $a_{tb} = 0.6$.

Calculation of Weight Average Branching Parameters

Number average branching parameters are available from experiments on T_g , eqs. (16)–(20).⁸ Then weight average branching parameters, needed for complete characterization of branched polymers, can be obtained, if \bar{n}_{bw} is calculated.

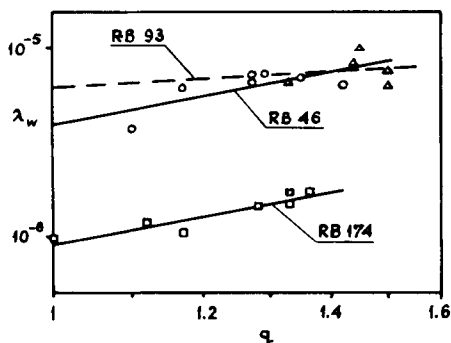


Fig. 6. Branching frequency λ_w vs. polydispersity degree $q = \bar{M}_w/\bar{M}_n$. Symbols are as in Figure 4.

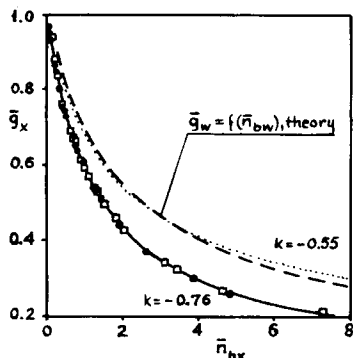


Fig. 7. Average branching degree \bar{g}_x vs. average number of branch points \bar{n}_{bx} . Randomly branched PS samples of Masuda et al.¹³: (●) $\bar{g}_n = f(\bar{n}_{bn})$; (□) $\bar{g}_w = f(\bar{n}_{bw})$ according to eq. (28) for $f = 4$ with $k = -0.76$. (—) Experimental data on PS in cyclohexane at 34.5°C, $\bar{g}_x = f(\bar{n}_{bx})$; (---) the theoretical Zimm-Stockmayer equation, $\bar{g}_w = f(\bar{n}_{bw})$, for $f = 4$.

Therefore, the ratio $\bar{n}_{bw}/\bar{n}_{bn}$ can be calculated from eq. (19) transformed into the following form:

$$\bar{n}_{bx,f} = \frac{1}{f-1} \left(\frac{\bar{M}_x}{\bar{M}_{x,\text{seg}}} - 1 \right) \quad (35)$$

Hence, assuming $\bar{M}_{n,\text{seg}} = \bar{M}_{w,\text{seg}}$ (it is valid for a statistically equal segment length), we obtain

$$\bar{n}_{bw}/\bar{n}_{bn} = (q-s)/(1-s) \quad (36)$$

where $s = \bar{M}_{\text{seg}}/\bar{M}_n$ is available from T_g measurements [eqs. (16)–(19)]. Also from eq. (19) or (35) we have another equivalent relation:

$$\bar{n}_{bw,f} = \frac{1}{f-1} \{q[(f-1)\bar{n}_{bn,f} + 1] - 1\} \quad (37)$$

Branching Frequency

Branching frequency λ_x , i.e., the average number of branch points per average molecular weight is defined by eq. (20):

$$\lambda_x = \bar{n}_{bx}/\bar{M}_x \quad (20)$$

For weight average parameters we have eq. (34) written as

$$\lambda_w = A_w q^{a_{2w}} \quad (38)$$

By combination of eqs. (20) and (38) we obtain

$$\lambda_n = A_n q^{a_{2n}} \quad (39)$$

where

$$A_w/A_n = \bar{n}_{bw}/\bar{n}_{bn} \quad (40)$$

and

$$a_{2n} = a_{2w} + 1 \quad (41)$$

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