

Analysis of Branched Poly(ethylene Terephthalate)*

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Synopsis

Poly(ethylene terephthalate) modified with 1,1,1-trishydroxymethyl propane (THP) and pentaerythritol was analyzed with respect to branching by combined GPC/viscometry measurements. The average effective functionality of the branching molecules was calculated and compared with the theoretically attainable functionality, thus permitting one to distinguish between different branching theories. Maximum effectiveness was achieved only at low concentrations of the modifiers added. Pentaerythritol and THP were found equivalent in the ratio 1:3, estimated from their influence on the polydispersities of the branched polyester. It was shown that apparent molecular weights obtained from GPC calibration with linear standards can be converted by correction factors. The resulting molecular weight averages of the branched PET samples were in a good agreement with those from the GPC/viscometry iteration procedure.

INTRODUCTION

Poly(ethylene terephthalate) (PET) is well known for its various applications in the fiber, film, and plastics industry. A simple way often used to modify the structure and the properties of PET is the incorporation of small amounts of tri- or tetrafunctional compounds. This readily leads to the formation of long chain branches.

In the papers published so far on the characterization of branched PET,^{1,2} standard techniques in molecular weight determination are used, i.e., light scattering, osmometry, and viscometry. With the new solvent mixture chloroform/hexafluoroisopropanol introduced recently,³ it is now possible to determine the long chain branching of PET by the combination of GPC measurements with viscometric data. This approach is an easy and effective method to get average molecular weights and molecular weight distribution of the branched sample as well as characteristic branching parameters.

THEORETICAL BACKGROUND

The Use of GPC and Viscometry in Determining Branching

The basic concept for the determination of branching by GPC is the universal calibration introduced by Benoit et al.^{4,5} They demonstrated that the hydrodynamic volume is proportional to the product of intrinsic viscosity $[\eta]$ and molecular weight M . Applying this concept to linear and branched

*Dedicated to Professor W. Hilger on the occasion of this 60th birthday.

molecules having the same elution volume leads to

$$M^{\text{lin}} \cdot [\eta]^{\text{lin}} = M^{\text{br}} \cdot [\eta]^{\text{br}} \quad (1)$$

Considering a branched and a linear molecule of the same molecular weight, the intrinsic viscosity of the branched sample is smaller than that of the linear one:

$$[\eta]^{\text{br}} = G \cdot [\eta]^{\text{lin}} \quad (G < 1) \quad (2)$$

where

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

g is the ratio of the mean squared radii of gyration referring to linear and branched molecules having the same molecular weight:

$$g = \langle R_G^2 \rangle_{\text{br}} / \langle R_G^2 \rangle_{\text{lin}} \quad (4)$$

Unfortunately, the value of the exponent b in eq. (3) is still in debate. Thurmond and Zimm⁶ in their early work on crosslinked polystyrene gave

$$b = 0.5 \quad (5)$$

while later Zimm and Kilb⁷ calculated

$$b = 1.5 \quad (6)$$

Both theories are valid only for theta solvents so that modifications are necessary for good solvents in which GPC measurements usually are carried out. Therefore, Kurata et al.^{8,9} took

$$b = 0.6 \quad (7)$$

while Zimm and Stockmayer¹⁰ proposed

$$b = 2 - a \quad (8)$$

where a is the exponent of the Mark-Houwink relation.

There are various experimental studies¹¹ in which values of $0.5 \leq b \leq 1.5$ have been found including variations of b depending on the type of sample.¹²

In their pioneering paper,¹⁰ Zimm and Stockmayer derived expressions for the parameter g . For randomly branched molecules with trifunctional branch points,

$$g_3 = \left[\left(1 + \frac{m}{7} \right)^{0.5} + \frac{4m}{9\pi} \right]^{-0.5} \quad (9)$$

and similarly for tetrafunctional branch points,

$$g_4 = \left[\left(1 + \frac{m}{6} \right)^{0.5} + \frac{4m}{3\pi} \right]^{-0.5} \quad (10)$$

m is the average number of branch points per molecule and is a function of the molecular weight M .

Drott and Mendelson¹³ in their treatment of GPC and viscosity data assumed that

$$m = \lambda \cdot M \quad (11)$$

Substituting the Mark-Houwink relation for linear molecules into eq. (2) with eq. (3) results in

$$[\eta]^{\text{br}} = k \cdot M^a \cdot g(M)^b \quad (12)$$

and for a polydisperse sample, respectively,

$$[\eta]^{\text{br}} = k \cdot \frac{\sum w_i \cdot M_i^a \cdot g(M_i)^b}{\sum w_i} \quad (13)$$

The following scheme can be used to determine branching from GPC and viscometric measurements^{9,13-15}:

1. The intrinsic viscosity of the branched sample, $[\eta]^{\text{br}}$, is measured.
2. The Mark-Houwink parameters k and a are known or have to be determined. With these parameters an apparent viscosity $[\eta]^{\text{app}}$ is calculated from GPC using eq. (13) with $g(M) = 1$ and $\lambda = 0$, respectively.
3. A computer program iterates λ in eq. (13) using eq. (9) or (10) and eq. (11) until $[\eta]^{\text{app}}$ equals $[\eta]^{\text{br}}$.
4. Once λ and therefore g is determined, the average molecular weights M_w^{br} and M_n^{br} as well as the corrected molecular weight distribution of the branched sample are calculated using the universal calibration.

Figure 1 gives an example on how intrinsic viscosity $[\eta]$, number average M_n , and weight average M_w vary with the parameter λ .

It should be pointed out that only the influence of long chain branching (LCB) can be detected by this proceeding because only LCB shows a remarkable effect in decreasing the viscosity $[\eta]$.

The Functionality of the Branching Molecule

If the amount of an added branching molecule is known and can be correlated to the parameter λ , it is possible to detect the branching effectiveness. As it will be shown below, this correlation allows also the examination of the theoretical models especially with respect to the value of exponent b in eq. (3).

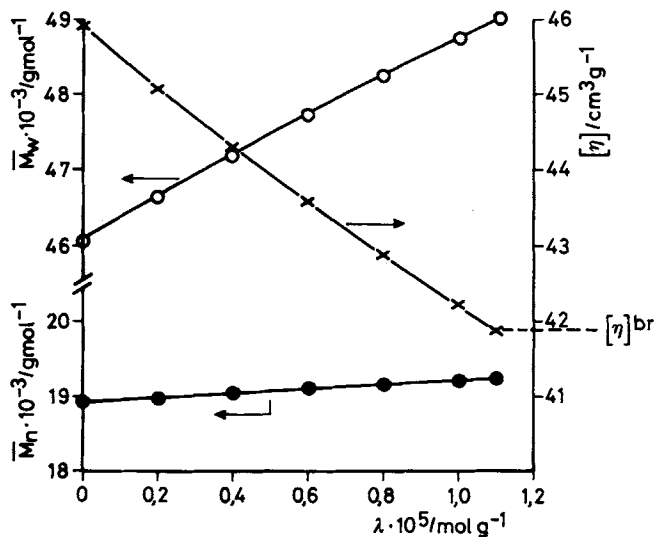


Fig. 1. Variation of the calculated M_w , M_n , and $[\eta]$ during the iteration procedure (sample 291).

The average number of branch points per macromolecule m , can be calculated from the number of branching molecules, n_b , and the number of branched polymer molecules, n , by

$$m = \frac{n_b}{n} = \frac{c_b}{M_b} \cdot M \quad (14)$$

c_b is the ratio of the mass of the branching molecule to the mass of the branched polymer (in g/g polymer), M_b and M are the molecular weights of the branching molecule and the polymer.

In the derivation of eq. (14) is implied that all added functional groups of the branching molecule result in a physically detectable branch. This assumption is not valid *a priori*. Therefore, eq. (14) is corrected by an efficiency factor ϕ ($0 \leq \phi \leq 1$):

$$m = \frac{c_b}{M_b} \cdot M \cdot \phi \quad (15)$$

ϕ can be interpreted as the number of effective (i.e., detectable) *branches* without consideration of the linear backbone of the chain.

From ϕ one can calculate the average effective functionality \bar{f}_{LCB} , which is caused by long chain branching. \bar{f}_{LCB} is the average number of *chains* starting from a branch point and including the backbone. For trifunctional branching molecules,

$$\bar{f}_{\text{LCB}} = \phi + 2 \quad (16)$$

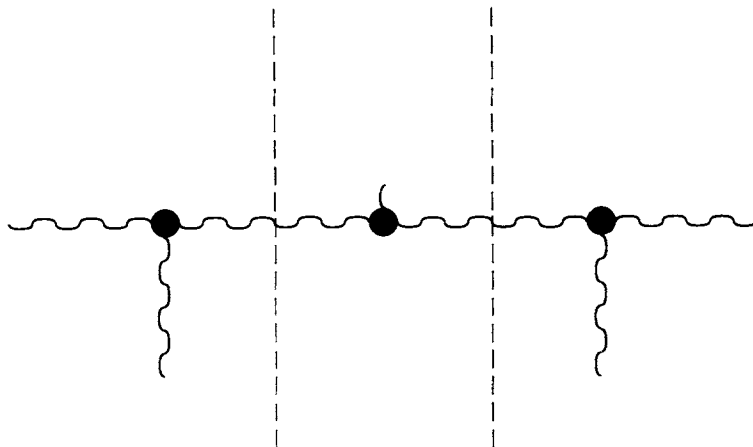


Fig. 2. Macromolecule with trifunctional branching, two branches effective: $\phi = (\text{effective branches})/(\text{possible branches}) = 2/3$; $\bar{f}_{\text{LCB}} = (\text{effective chains starting from the branch points})/(\text{branch points}) = 8/3$.

and for tetrafunctional molecules,

$$\bar{f}_{\text{LCB}} = 2 \cdot \phi + 2 \quad (17)$$

The factor 2 in eq. (17) takes into account that two branches are starting from one branch point. Figure 2 illustrates eq. (16).

Correlating eqs. (15), (16), or (17) and eq. (11) leads for trifunctional branching molecules to

$$\bar{f}_{\text{LCB}} = \lambda \cdot \frac{M_b}{c_b} + 2 \quad (18)$$

and for tetrafunctional branching molecules to

$$\bar{f}_{\text{LCB}} = 2 \cdot \lambda \cdot \frac{M_b}{c_b} + 2 \quad (19)$$

For the limiting case $\lambda = 0$, i.e., $m = 0$ (no branching), the expected result $\bar{f} = 2$ is given, meaning linear chains.

The derivation above leads to eqs. (18) and (19) also for polydisperse samples just by substituting M by the number average molecular weight \bar{M}_n .

EXPERIMENTAL

Polymer Preparation

PET was prepared from dimethyl terephthalate and glycol using manganese and antimony as catalysts. All branching modifiers were added to the transesterification. The use of a pilot line containing an exactly calibrated torque meter allowed the preparation of samples having different modifier contents but the same melt viscosity.

Analyses

The GPC measurements in chloroform/hexafluoroisopropanol (98 : 2 vol %) were carried out as described earlier.³ In the same solvent system, the intrinsic viscosities $[\eta]^{br}$ were determined using the Huggins extrapolation. Because of their importance in the calculation of parameter λ , only measurements with $r > 0.99$ were accepted. Repeated measurements proved that no degradation took place within eight hours.

To determine the content of pentaerythritol (Penta) and 1,1,1-trihydroxymethyl propane (THP), the polyesters were totally degraded by methanolysis. After derivatization with acetic anhydride, THP and Penta were quantitatively analyzed by gas chromatography.

RESULTS AND DISCUSSION

Influence of the Exponent b

Most of the studies on the GPC analysis of branched polymers published so far are dealing with polyethylene (PE). For polymerizates like PE, it is difficult to get additional information about the degree of branching. It is the advantage of analyzing a polycondensate that branching is not a side reaction but a main reaction involved in the normal polycondensation mechanism. Furthermore, the amount of branching molecules is known or can be determined which finally allows to compare results from different theories.

Thus, different values of b in eq. (4) were taken and the GPC/viscosity data were treated as described. The results for one trifunctional and one tetrafunctional branched sample are given in Table I.

It was found that the influence of the value of b on molecular weight averages and polydispersity is negligible within the experimental error of GPC. Although the deviation from the Schulz-Flory distribution with an expected $M_w/M_n = 2$ is significant, the polydispersities are rather small in comparison to what is detected on PE.

TABLE I
Influence of the Value of b on Molecular Weight Averages and Branching Parameters

b	M_w^{br} (g mol ⁻¹)	M_n^{br} (g mol ⁻¹)	M_w^{br}/M_n^{br}	M_z^{br} (g mol ⁻¹)	$\lambda \times 10^5$ (mol g ⁻¹)	\bar{f}_{LCB}	\bar{f}_{max}
Sample 291 modified with 0.20 wt % THP							
0.5	48,957	19,263	2.54	88,954	3.34	4.2	3
0.6	48,966	19,255	2.54	89,148	2.65	3.8	3
2 - α^a	49,022	19,237	2.55	89,868	1.11	2.7	3
1.5	49,025	19,234	2.55	89,957	0.92	2.6	3
Sample 575 modified with 0.06 wt % Penta							
0.5	55,135	21,230	2.60	111,023	1.04	6.7	4
0.6	55,149	21,224	2.60	111,319	0.83	5.7	4
2 - α^a	55,200	21,205	2.60	112,309	0.35	3.6	4
1.5	55,205	21,202	2.60	112,419	0.29	3.3	4

^a $\alpha = 0.731$.

Since the calculated molecular weights are so close, it is impossible to differentiate between theoretical values of b by light scattering or osmometry, even for samples with a higher content of branching molecules. On the other hand, calculating the average functionalities, \bar{f}_{LCB} and comparing them with the maximum functionalities possible leads to the conclusion that values of $b = 0.5$ or 0.6 are not appropriate. Taking into account that all measurements were carried out in a good solvent, $b = 2 - a$ was taken for further calculations.

Trifunctional Branching by Trishydroxymethylpropane (THP)

THP served as a model compound to check on the influence of the polycondensation time and the concentration of a trifunctional branching molecule. Thus, a prepolymer containing 0.52 wt % THP was prepared. Portions of it were then polycondensated to different viscosities and analyzed with respect to branching (Table II). The polydispersity of the branched polymer increases strongly with longer reaction time, i.e., with increasing viscosity of the sample. In contrast, the average functionality \bar{f}_{LCB} remains constant. It can also be seen from repeated measurements that \bar{f}_{LCB} is rather insensitive to changes in the parameter λ .

From these results it seems likely that all potential branches are formed early in the polycondensation if not already during the transesterification. Growing of the branches then leads to the observed increase in polydispersity. The influence of the amount of THP added was also investigated. Therefore, samples of equal melt viscosity were prepared and analyzed (Table III). As expected, the polydispersity increased reaching unusually large values at high concentrations of THP. The calculated effective functionalities \bar{f}_{LCB} , however, show a decrease with increasing THP content. Apparently, all three possible branches of THP are effective only at very low concentrations.

At higher concentrations it becomes more possible that the macromolecules contain more than one branch point. This is the case especially for sample 295 where the number of THP molecules exceeds the average number of macromolecules. Regarding its coil-like structure, it seems plausible that a macromolecule with more than one branch point cannot grow that easily. In turn, this might lead to the observed decrease in the effective functionality. There

TABLE II
Influence of the Polycondensation Time t_{pc} (0.52 wt % THP)

Sample	t_{pc} (min)	$[\eta]^{br}$ ($\text{cm}^3 \text{g}^{-1}$)	M_w^{br} (g mol^{-1})	M_n^{br} (g mol^{-1})	M_w^{br}/M_n^{br}	$\lambda \times 10^5$ (mol g^{-1})	\bar{f}_{LCB}
307	165	24.9	22,000	9900	2.22	1.20	2.3
			22,400	10,100	2.22	1.43	2.4
309	174	32.0	34,300	13,500	2.54	1.54	2.4
			33,950	13,750	2.47	1.50	2.4
506	180	38.0	45,800	16,300	2.81	1.42	2.4
			45,600	16,400	2.74	1.41	2.4
313	193	42.1	57,750	16,850	3.43	1.41	2.4
			56,900	16,850	3.38	1.38	2.4

TABLE III
Influence of the Amount of THP on Molecular Weight Averages and Effective Functionality \bar{f}_{LCB}

Sample	Content (wt %)	$[\eta]^{br}$ ($\text{cm}^3 \text{g}^{-1}$)	M_w^{br} (g mol^{-1})	M_n^{br} (g mol^{-1})	M_w^{br}/M_n^{br}	$\lambda \times 10^5$ (mol g^{-1})	\bar{f}_{LCB}
289	0	46.1	46,350	22,700	2.04	—	—
290	0.08	44.3	47,350	20,750	2.28	0.51	2.9
			46,800	20,551	2.28	0.45	2.8
291	0.20	41.9	49,000	19,250	2.55	1.11	2.7
			49,250	19,550	2.52	1.16	2.8
292	0.26	41.7	51,550	18,700	2.76	1.32	2.7
			50,050	18,300	2.73	1.19	2.6
293	0.30	41.6	51,800	17,950	2.88	1.27	2.6
294	0.31	42.6	50,700	16,900	3.01	0.86	2.4
313	0.52	42.1	57,750	16,850	3.43	1.41	2.4
295	0.90	43.2	68,900	15,250	4.52	1.49	2.2

is, of course, the possibility of short chain branching which is not covered by the GPC/viscosity method applied here.

Although there is some evidence for sterical hindrance to explain the decrease of \bar{f}_{LCB} , the limitations of the theoretical background should be kept in mind. In the original Drott equation [eq. (11)], λ is assumed independent of the molecular weight M . This assumption is doubted by some authors,^{16,17} leading to a modification of eq. (11) by introducing an exponent for M . But, without a further method of determine λ , such an approach cannot be validated.

Tetrafunctional Branching by Pentaerythritol

As an example for tetrafunctional branching, Penta was used. Table IV gives the results calculated with g_4 [eq. (10)]. Again one observes an increase in polydispersity with increasing amount of Penta, but the theoretically

TABLE IV
Influence of the Amount of Penta on Molecular Weight Averages
and Effective Functionality \bar{f}_{LCB}

Sample	Content (wt %)	$[\eta]^{br}$ ($\text{cm}^3 \text{g}^{-1}$)	M_w^{br} (g mol^{-1})	M_n^{br} (g mol^{-1})	M_w^{br}/M_n^{br}	$\lambda \times 10^5$ (mol g^{-1})	\bar{f}_{LCB}
8830	0	48.0	48,500	24,000	2.02	—	—
8831	0.025	46.9	50,600	22,900	2.21	0.18	4.0
			50,400	22,500	2.24	0.17	3.9
575	0.06	45.8	55,200	21,200	2.60	0.35	3.6
			54,800	21,150	2.59	0.35	3.6
9954	0.08	44.7	54,050	20,300	2.66	0.39	3.3
			54,800	20,500	2.68	0.40	3.4
528	0.11	43.8	58,800	20,250	2.90	0.56	3.4
			58,800	20,300	2.90	0.55	3.3
509	0.15	41.4	60,900	17,700	3.37	0.75	3.4
			60,500	17,500	3.38	0.75	3.4

possible functionality is reached only at very low concentrations. Repeated GPC measurements illustrate the good reproducibility.

Comparison of the Influence of THP and Penta on MWD

From the results presented above it was possible to detect what amount of Penta is equivalent to a given amount of THP. Recently, Langla and Strazielle² reported an equivalence of 0.1 mol % Penta to 0.4 mol % THP by using the ratio $G = [\eta]^{br}/[\eta]^{lin}$ for their calculation. Because of the small differences in G and the experimental errors in its determination, this method can be considered only a rough estimation.

A better estimation can be made from the influence of the branching molecule on the polydispersity of the polymer. Such an approach is less susceptible to errors and takes into account that the samples have a molecular weight distribution rather than relying on only one average, e.g., intrinsic viscosity.

In Figure 3 the polydispersities from Tables III and IV are plotted against the content of THP and Penta in the polymer. An equivalence of 1 : 3 (0.1 wt % Penta ~ 0.3 wt % THP) is found. Because the molar masses of Penta and of THP are very close, the same equivalence results by using mol % instead of wt %.

It should be noted that all samples taken are of nearly the same melt viscosity ($\eta_{295^\circ\text{C}}$ approximately 270 Pa s) due to the method of their preparation. Possible differences in the melt viscosity of about $\pm 10\%$ lead to polydispersity changes of approximately ± 0.1 , which is within the limits of the estimation above.

Prediction of GPC Behavior of Randomly Branched Polymers

An interesting approach to calculate molecular weight averages of branched samples is given by Shultz.¹⁸ Using the GPC calibration derived from un-

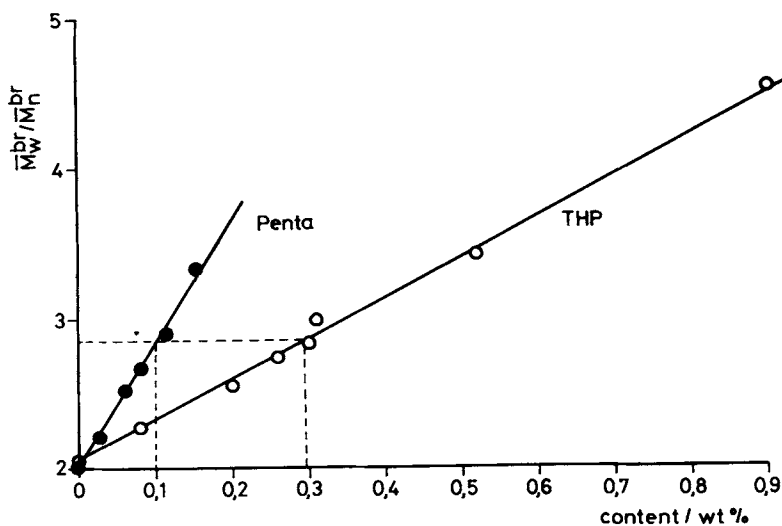


Fig. 3. Comparison of THP and Penta effecting the polydispersity of the branched sample.

branched samples, apparent molecular weight averages are received and converted by correction factors. These correction factors were generated by a mathematical treatment on polymers formed by random condensation with tri- or tetrafunctional branching. The method is based on the MWD functions of Stockmayer¹⁹ and on the expressions for g [eqs. (9) and (10)].¹⁰ No viscosity measurements and no iterative procedure are necessary.

Our data of tri- and tetrafunctional branched polyesters seemed to be favorable to test the approach of Shultz. From the apparent polydispersity derived from GPC, the branching index γ was calculated. Tables 1 and 2 in Ref. 18 had been extended for the Mark-Houwink exponent $\alpha = 0.731$ (as determined for the GPC solvent³) and were used for interpolation.

The polydispersity of the branched samples, $M_w^{\text{br}}/M_n^{\text{br}}$, as well as $M_z^{\text{br}}/M_w^{\text{br}}$ was calculated from γ :

$$\frac{M_w^{\text{br}}}{M_n^{\text{br}}} = \frac{2}{1-\gamma} \cdot \left(1 - \frac{\gamma}{3}\right) \quad (20)$$

$$\frac{M_z^{\text{br}}}{M_w^{\text{br}}} = \frac{3-\gamma}{2(1-\gamma)} \quad (21)$$

for trifunctional branching and

$$\frac{M_w^{\text{br}}}{M_n^{\text{br}}} = \frac{2}{1-\gamma} \cdot \left(1 - \frac{\gamma}{4}\right) \quad (22)$$

$$\frac{M_z^{\text{br}}}{M_w^{\text{br}}} = \frac{3}{2(1-\gamma)} \quad (23)$$

for tetrafunctional branching.

TABLE V
Polydispersities Calculated Using the Shultz Method and the Iteration Procedure (in Parentheses)

Sample	$M_w^{\text{app}}/M_n^{\text{app}}$	γ	$M_w^{\text{br}}/M_n^{\text{br}}$	$M_z^{\text{br}}/M_w^{\text{br}}$
290 ^a	2.24	0.17	2.27 (2.28)	1.66 (1.70)
291	2.43	0.28	2.52 (2.55)	1.89 (1.83)
292	2.60	0.35	2.72 (2.76)	2.04 (2.03)
293	2.71	0.39	2.85 (2.88)	2.14 (2.16)
294	2.87	0.44	3.08 (3.01)	2.29 (2.35)
313	3.14	0.51	3.39 (3.43)	2.54 (2.66)
295	3.98	0.65	4.48 (4.52)	3.69 (3.36)
8831 ^b	2.19	0.13	2.22 (2.21)	1.72 (1.68)
575	2.49	0.29	2.61 (2.60)	2.11 (2.03)
9954	2.54	0.31	2.67 (2.66)	2.17 (2.11)
528	2.69	0.37	2.88 (2.90)	2.38 (2.53)
509	3.02	0.47	3.33 (3.37)	2.83 (2.73)

^a THP containing samples from Table III.

^b Penta containing samples from Table IV.

The results of Table V are in excellent agreement with the results from the iteration method using combined viscosity and GPC data. It points to the validity of the Drott-Mendelson approach, especially with respect to eq. (11). Shultz used a value of $b = 0.5$ for his calculations. This seems to be in contrast to $b = 2 - a$ used for the iteration procedure, but as it was shown in Table I the influence of b on molecular weight averages is small.

Therefore, if the parameter λ and the true molecular weight distribution are not of interest, the method of Shultz easily leads to reliable molecular weight averages of branched polycondensates.

CONCLUSION

The analysis of combined data from GPC and viscometry is the most applicable way to treat long chain branching in polymers. Unfortunately, the theoretical background is not yet understood completely. The main discrepancies focus on the equation

$$G = g^b$$

Not only is the value of b disputed, including its variation in between the theoretical limits of 0.5 and 1.5 (refer to the discussion above). Also, different expressions for g are used, sometimes in combination with varying the value of b .²⁰⁻²⁴ In spite of this, eqs. (9) and (10) seem to comprise the most convincing approach. They are generalized functions without a restriction of the number of branching units.¹⁰ In addition, they have been proved superior to other relations by theoretical calculations.²⁵

In the study presented here, a randomly branched polycondensate with tri- and tetrafunctional branches has been analyzed. From calculation of the average functionalities of the branching molecules, a correct description of the experimental results was received by using eq. (9) and (10) with $b = 2 - a$ and 1.5, respectively. Interestingly, the latter solution describes the results in the original paper of Drott and Mendelson²⁶ just as well.

By the alternative model of Shultz¹⁸ the molecular weight averages of the branched samples can be calculated from GPC data solely.

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References

1. P. Manaresi, A. Munari, F. Pilati, G. C. Alfonso, S. Russo, and M. L. Sartirana, *Polymer*, **27**, 955 (1986).
2. B. Langla and C. Strazielle, *Makromol. Chem.*, **187**, 591 (1986).
3. K. Weisskopf, *J. Polym. Sci. Polym. Chem. Ed.*, **26**, 1919 (1988).
4. H. Benoit, Z. Grubisic, P. Rempp, D. Decker, and J. G. Zilliox, *J. Chim. Phys.*, **63**, 1507 (1966).
5. Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci. B.*, **5**, 753 (1967).
6. C. D. Thurmond and B. H. Zimm, *J. Polym. Sci.*, **8**, 477 (1952).
7. B. H. Zimm and R. W. Kilb, *J. Polym. Sci.*, **23**, 19 (1959).
8. M. Kurata, M. Abe, M. Iwama, and M. Matsushima, *Polym. J.*, **3**, 729 (1972).
9. M. Kurata, H. Okamoto, M. Iwama, M. Abe, and T. Homma, *Polym. J.*, **3**, 739 (1972).
10. B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301 (1949).
11. P. A. Small, *Adv. Polym. Sci.*, **18**, 1 (1975).
12. D. C. Bugada and A. Rudin, *Eur. Polym. J.*, **23**, 847 (1987).

13. E. E. Drott and R. A. Mendelson, *J. Polym. Sci. A-2*, **8**, 1361 (1970).
14. M. R. Ambler, R. D. Mate, and J. R. Purdon, Jr., *J. Polym. Sci. Polym. Chem. Ed.*, **12**, 1759 (1974).
15. M. M. Coleman and R. E. Fuller, *J. Macromol. Sci. B*, **11**, 419 (1975).
16. A. Cervenka and G. R. Williamson, *Eur. Polym. J.*, **10**, 305 (1974).
17. E. P. Otocka, R. J. Rose, M. Y. Hellmann, and P. M. Muglia, *Am. Chem. Soc. Polym. Prepr.*, **12**, 274 (1971).
18. A. R. Shultz, *Eur. Polym. J.*, **6**, 69 (1970).
19. W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943); **12**, 125 (1944).
20. J. A. Cote and M. Shida, *J. Polym. Sci. A-2*, **9**, 421 (1971).
21. L. Wild, R. Ranganath, and A. Barlow, *J. Appl. Polym. Sci.*, **21**, 3331 (1977).
22. L. Westerman and J. C. Clark, *J. Polym. Sci. Polym. Phys. Ed.*, **11**, 559 (1973).
23. M. R. Ambler, *J. Appl. Polym. Sci.*, **21**, 1655 (1977).
24. D. Lecacheux, J. Leseq, and C. Quivoron, *J. Appl. Polym. Sci.*, **27**, 4867 (1982).
25. M. Hoffmann and R. Kuhn, *Makromol. Chem.*, **174**, 149 (1973).
26. E. E. Drott and R. A. Mendelson, *J. Polym. Sci. A-2*, **8**, 1373 (1970).

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