

# High Molecular Weight Tail and Long-Chain Branching in Low-Density Polyethylenes

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**ABSTRACT:** The composition of the high molecular weight tail in branched low-density polyethylenes made by both tubular and autoclave reactors was studied in detail using size-exclusion chromatography (SEC) coupled with a viscosity detector (VD) and a two-angle light-scattering detector (LSD). The detection of a second peak at very small elution volumes in the light-scattering chromatogram but not in the refractive index chromatogram and viscosity chromatogram is due to high molecular weight species. It is also indicative of a change in the long-chain branching distribution. It was found that the intrinsic viscosity contraction factor  $g'$  scales with the radius of the gyration contraction factor,  $g$ , with the exponent,  $\varepsilon$ , having a value in the range 0.4–1.4. Furthermore,  $\varepsilon$  shows significant molar mass dependence. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2815–2822, 2001

**Key words:** size-exclusion chromatography; polyethylene; long-chain branching; viscosity detector; radius of gyration; molecular structure

## INTRODUCTION

In a recent publication, we showed that the detection of a second peak in the light-scattering (LS) chromatogram of the standard reference low-density polyethylene (LDPE) SRM 1476 is due to high molecular weight species.<sup>1</sup> While evidence of branching was observed across the whole molecular weight distribution, a significant densification was seen for  $M > 10^6$  as the radius of gyration approaches a plateau at  $\sim 52$  nm. In the same region, the equivalent unbranched polymer gives radii of gyration  $> 300$  nm. The molecules in this high molecular weight region of SRM 1476 are highly branched and compacted.

High molecular weight tails<sup>2–5</sup> comprising highly branched molecules are notoriously diffi-

cult to detect due to insufficient sensitivity of the differential refractometer (DRI) at low concentrations at the very end of the molecular weight distribution. The viscosity detector (VD) also shows inherent detection limits at low polymer concentrations and low intrinsic viscosities (IVs) as discussed later in this article. However, high molecular weight tails in LDPEs can have a strong influence on the rheological and physical properties and, therefore, their presence needs to be detected.<sup>4</sup>

Commercial polyethylenes (PEs) are produced by two very different processes—tubular and autoclave. Polymers from these two processes have been reported to differ in molecular weight distribution and degree, structure, and distribution of long-chain branching (LCB).<sup>6</sup>

In a tubular reactor, the temperature is not constant, but increases between the beginning and the end of the reaction zone along the tube. The molecules initiated first grew at low temperatures and low conversions and, therefore, show

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less LCB than that of the total polymer. When passing into reactor zones where the temperatures and conversions are higher, these molecules undergo transfer reactions leading to increased molecular weights and higher numbers of LCBs than in the original molecules.

In a stirred autoclave reactor at constant pressure, temperature, and conversion, the LCB points are distributed essentially at random along the chains irrespective of molecular weight. Tubular-made resins were characterized by comblike branching, while autoclave products were shown to have treelike LCB, leading to nearly globular shapes in solutions.

In this article, the molecular structures of tubular and autoclave resins were examined using a size-exclusion chromatograph (SEC) coupled with a LS detector (LSD) and a VD. The samples were analyzed in terms of molecular weight composition, radius of gyration, and LCB. Whether both grades can exist with a high molecular weight tail has not been verified experimentally and was the subject of the present article.

## EXPERIMENTAL

### Instrumentation

The SEC used in this study consisted of a Waters Associates 150CV equipped with a Waters DRI, a Precision Detector PD2040 two-angle, 15° and 90°, a laser LSD, and a Viscotek model 150R differential bridge VD. All the detectors were installed in the column oven compartment together with a set of four columns comprising three Shodex columns (AT806M/S, UT807S, AT804S) and a Waters column (Styragel HR2).

The experiments were undertaken with a flow rate of 1.0 mL min<sup>-1</sup> at 140°C and trichlorobenzene as an eluant. A 5- $\mu$ m on-line filter was connected in front of the columns. The 10- $\mu$ L flow-through cell of the LSD was connected immediately after the columns. The DRI and VD were connected in parallel behind the LSD. The ratio of the volume of flow between the DRI and VD lines was approximately 50:50. An injection volume of 400  $\mu$ L was employed throughout. The columns were calibrated using 22 polystyrene standards supplied by Polymer Laboratories with molecular weights ( $M$ ) ranging from 2050 to 4,000,000. Data handling was accomplished using the Viscotek TriSEC software and Precision Detectors software packages.

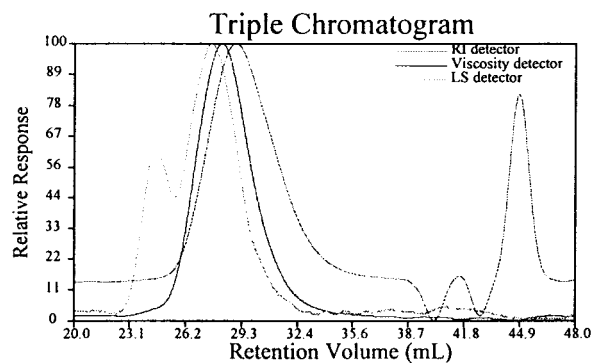
Performance of the VD was confirmed from the Mark-Houwink coefficients for polystyrene (PS) derived from Universal Calibration. The values of ( $\alpha = 0.67$  and  $k = 1.81 \times 10^{-4}$  compare well with the figures of 0.67 and  $1.75 \times 10^{-4}$  quoted in the *Polymer Handbook* (3rd ed.).<sup>7</sup> The LSD was calibrated using a standard PS of  $M = 65,000$  and then its performance was assessed by measuring the molecular weights of 22 PS standards. The values were found to agree with the quoted values from Polymer Laboratories to better than 5%.

### Sample Preparation

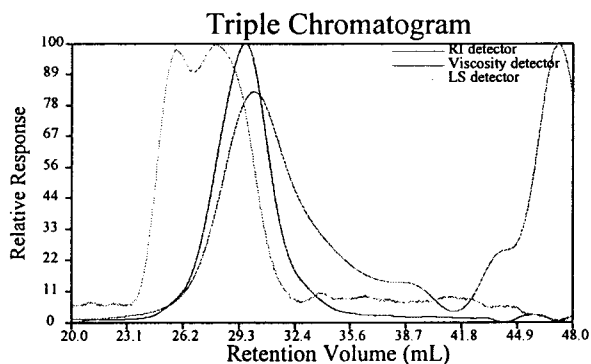
For comparison with SRM 1476, a commercial linear HDPE produced by BP Chemicals (Grange-mouth, UK) with an  $M_w$  of 370,000 was employed. All solutions were prepared in filtered 1,2,4-trichlorobenzene containing 0.1 wt % of an antioxidant (Santonax R) to prevent oxidative degradation of the polymer. This was the same solvent used as the SEC eluant. The SRM 1476 was prepared by dissolving  $\sim 20$  mg of polymer in 20 mL of the solvent. Dissolution of the sample was achieved in an oven at 160°C for 5 h. The HDPE solution was prepared by dissolving 6 mg of polymer in 20 mL of the eluant using a dissolution time of 7 h at 160°C. Dissolution for the PS standards was performed at 160°C for 1 h to prevent degradation.

## RESULTS AND DISCUSSION

Four commercial LDPEs and branched standard PE, SRM 1476, were used in the study. In addition, two linear PEs were included for comparative purposes: standard reference material SRM 1475 and an HDPE ( $M_w \sim 360,000$ ). Polymers T1



**Figure 1** Chromatograms for SRM 1476 obtained by LSD, VD, and DRI.

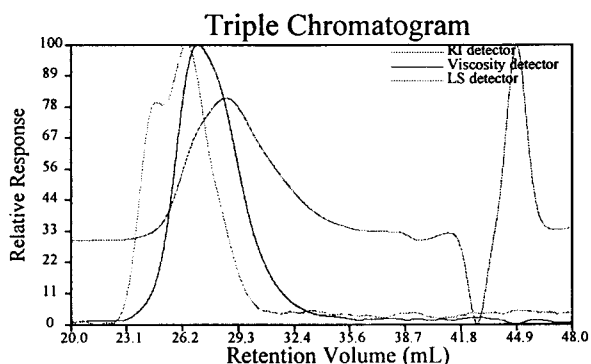


**Figure 2** Chromatograms for polymer T1 obtained by LSD, VD, and DRI.

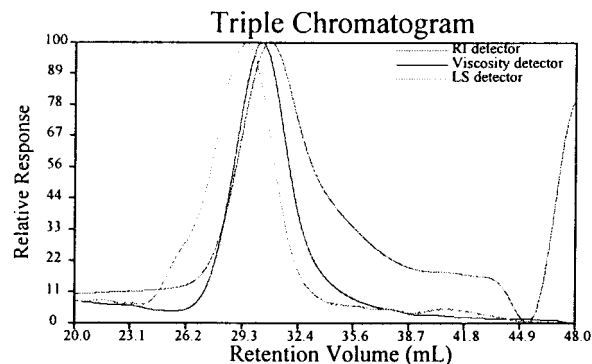
and T2 and SRM 1476 were made by a high-pressure free-radical polymerization process in a tubular reactor while polymers A1 and A2 were synthesized in a stirred autoclave reactor.

The tubular resins SRM 1476 and polymers T1 and T2 show a second peak in the LSD chromatogram for the 15° angle at very small elution volumes which is not detected in the DRI and VD chromatograms (Figs. 1–3, respectively). While the autoclave grade A1 has a small shoulder in the LS chromatogram (Fig. 4), polymer A2 shows only a single peak (Fig. 5).

The difference in response between the LSD and the VD merely reflects the difference in sensitivity. The LSD signal is proportional to  $cM$  ( $c$  = concentration), while the VD response is proportional to  $cM^\alpha$ , where  $\alpha$  is the Mark–Houwink parameter. For linear PE,  $\alpha$  is  $\sim 0.7$ ; however, for the high molecular weight tail of the branched PEs studied in this article,  $\alpha$  approaches 0 as illustrated in Figure 6. This results in a much reduced response for the viscometer. The DRI responds according to  $c$ .



**Figure 3** Chromatograms for polymer T2 obtained by LSD, VD, and DRI.



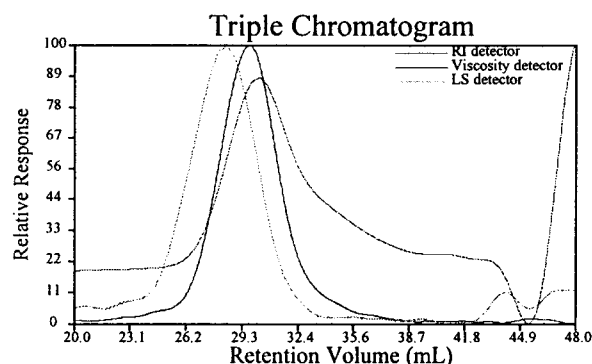
**Figure 4** Chromatograms for polymer A1 obtained by LSD, VD, and DRI.

A plot of  $\log M$ , obtained by LS, as a function of the retention volume is shown in Figure 7 for the LDPEs. Also included in this figure are the two linear PEs.

The molecules of the tubular grades SRM 1476 and T2 eluting from the columns below a retention volume of 26 mL have extreme high molecular weights and show a deviation from the linear molecular weight–retention volume relationship above a retention volume of 26 mL. The grade T1 shows the same trend as for T2 and is excluded for clarity.

This sharp change in slope of the LSD plots is indicative of a change in the molecular structure and LCB concentration in species below and above the 26 mL retention volume. We submit that the lower retention volume fraction in SRM 1476, T1, and T2 has not only a higher molecular weight but also a higher concentration of LCBs.

The two autoclave samples A1 and A2 do not have such high molecular weight molecules as those of the tubular grades. Sample A1, which has



**Figure 5** Chromatograms for polymer A2 obtained by LSD, VD, and DRI.

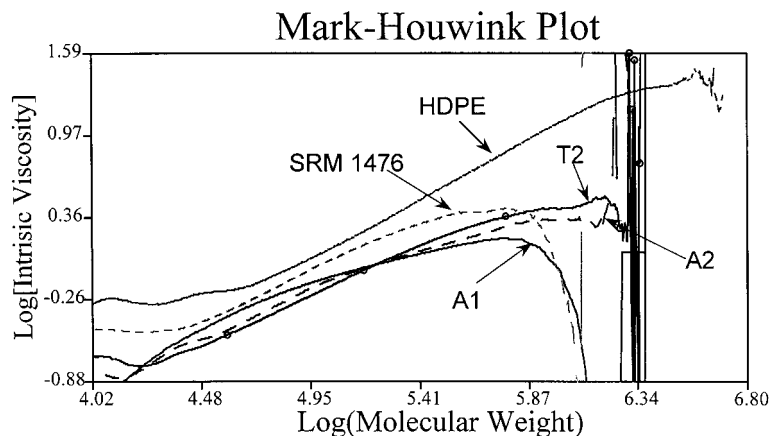


Figure 6 Mark Houwink plot for SRM 1476, A1, A2, T2, and HDPE.

a small shoulder in the LS chromatogram, shows an upturn similar in kind to that of the tubular resins, whereas the A2 material has a much more linear curve.

The radius of gyration gives an important insight into the structure of the molecules in the high molecular weight region and  $R_g$  values are shown in Figure 8 together with the unbranched HDPEs. The radius of the gyration relationship was determined from linear HDPE to be

$$R_g = 0.025M^{0.564}$$

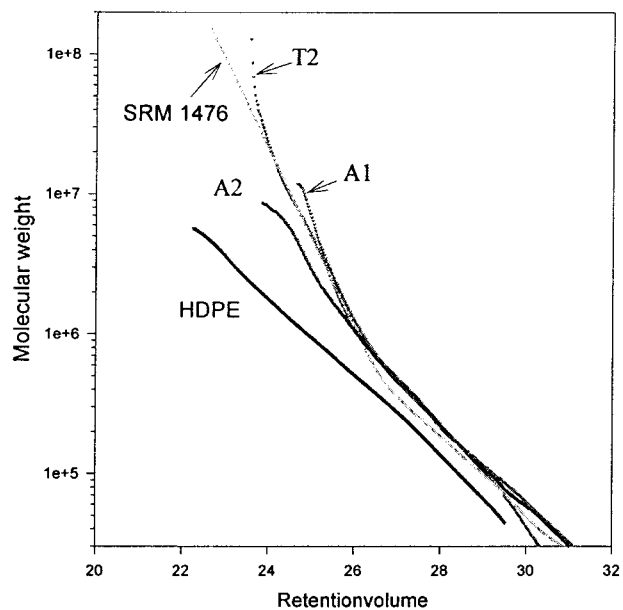


Figure 7 Molecular weight versus retention volume for A1, A2, T2, SRM 1476, and a linear HDPE.

The value is in perfect agreement with that theoretically predicted from the Fox-Flory equation:

$$[\eta] = 6^{3/2} \phi R_g^{3/2} M^{-1}$$

with  $\phi$  the universal constant ( $2.1 \pm 0.4 \times 10^{21}$  dL mol<sup>-1</sup> cm<sup>-3</sup>). The Mark-Houwink equation for linear PE in TCB at 140° was found:

$$[\eta] = 4.82 \times 10^{-4} M^{0.707}$$

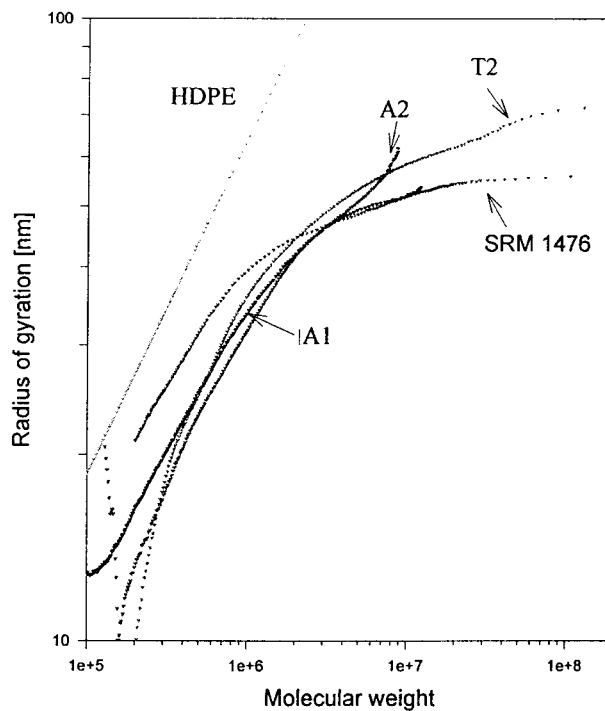


Figure 8 Radius of gyration versus molecular weight for A1, A2, T2, SRM 1476, and a linear HDPE.

**Table I**  $\epsilon$  Values for LDPES from the Literature

Work by	Method	No. Samples	$\epsilon$	LDPE	Molar Mass Dependence	Ref.
Hert and Strazielle	VD, LSD, off-line	1	0.5–1	Tubular	Strong	12
		1	0.5–1	Autoclave	Strong	
		1	0.8–1	Autoclave	Weak	
Arndt et al.	VD, LSD, off-line	1	0.4–1.1	—	Strong	13
Bugada and Rudin	SEC–VD; $^{13}\text{C}$ -NMR	3	0.42–0.73	Tubular	—	14
		5	0.66–1.04	Autoclave	—	
Tackx and Tacx	SEC–LSD	1	1–1.8	Tubular	Strong	8
		1	1–1.5	Autoclave	Strong	

The combination of the last two equations relates  $R_g$  with the molar mass:

$$R_g = 0.025M^{0.569}$$

Relationships of  $R_g$  and  $\eta$  with the molar mass are in agreement with results obtained recently by Tackx and Tacx.<sup>8</sup>

For  $2 \times 10^5 < M < 10^6$ , the radius of gyration of all LDPES increases in a linear rate. Second, for  $M > 10^6$ , a dramatic change in shape is observed. In this region, the radius of gyration of SRM 1476, T1 (not shown), T2, and A1 increases only very slightly with evidence of a plateau between 50 and 70 nm. This indicates a “densification” process which can be accounted for in terms of an increasing LCB concentration. The A2 grade does not show such a densification.

The relationship between the IV and the radius of gyration branching factors,  $g'$  and  $g$ , is commonly described as

$$g' = g^\epsilon$$

The branching index  $\epsilon$  is a sensitive sonde for the segment (or chain) density distribution in the domain of the molecule.<sup>10</sup> The value is directly related to the branching structure and number of LCBs. Theoretically predicted values for the branching index  $\epsilon$  are between 0.5 and 1.5.<sup>9</sup> If the hydrodynamic radius (viscometric size) was proportional to the radius of gyration independently of whether the molecule was branched or linear, it would follow that

$$g' = g^{3/2}$$

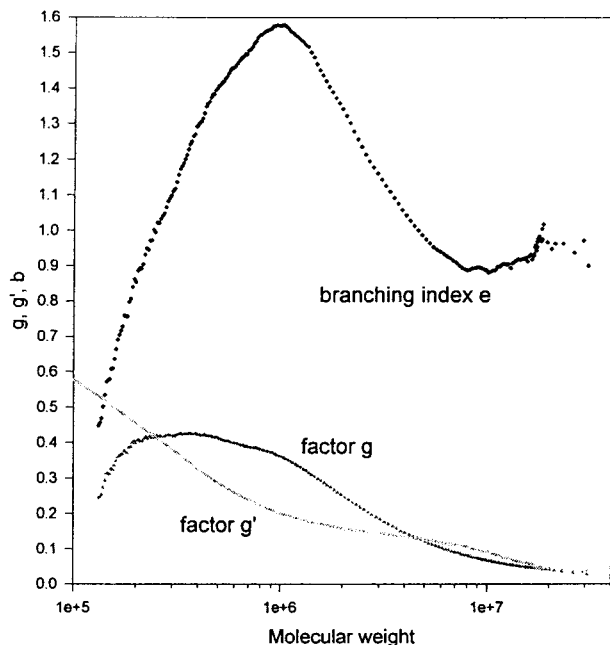
Berry and Orofino assumed that in the case of combs with relatively short LCBs a value of  $\epsilon = 3/2$  is applicable.<sup>11</sup> The increase in segment density in the polymer domain due to branching changes the relationship between the viscometric size and the radius of gyration, leading to a value for  $\epsilon$  of less than 3/2.

Lower values than  $\epsilon = 3/2$  of the exponent also indicate that the viscometric size is less sensitive to the effect of branching than is the radius of gyration. The 1/2 scaling was found to be valid for star-shaped molecules or molecules with treelike branching.

Several researchers experimentally tried to determine  $\epsilon$  values for LDPES. But, often,  $\epsilon = 0.5$  was used without further experimental confirmation to convert  $g'$  values, obtained from IV measurements, into  $g$  values, which then were used to calculate numbers of LCBs per molecule by means of the Stockmayer and Zimm equation.<sup>10</sup>

Experimentally obtained  $\epsilon$  values for LDPES from the literature are summarized in Table I. Tubular and autoclave resins (Table I) do not show particular differences in  $\epsilon$  values which span the whole theoretically predicted range. Work by Hert and Strazielle,<sup>12</sup> Arndt et al.,<sup>13</sup> and Tackx and Tacx<sup>8</sup> indicates that  $\epsilon$  is a function of molar mass.

The data for the branching factors,  $g$  and  $g'$ , and the branching index,  $\epsilon$ , from polymers T2, A1, and A2 are shown in Figures 9–11. The branching index  $\epsilon$  shows significant molar mass dependence on the polymers regardless of the origin of the



**Figure 9** Molecular weight dependence of the branching indices  $g$ ,  $g'$ , and  $e$  of LDPE T2.

LDPE. Between  $2 \times 10^5$  and  $4 \times 10^5$  molecular weight, the branching index  $\epsilon \sim 1/2$  and increases strongly with increasing molecular weight of the polymer. Values for  $\epsilon$  reach a plateau at values of 1.3–1.4. A slight decrease of  $\epsilon$  values was found for T2 beyond 1 Mio molecular weight. The  $\epsilon$  values in the range of  $2 \times 10^5$  and  $4 \times 10^5$  molecular weight, which contains most of the polymer's material, are in close agreement with the results obtained by Hert and Strazielle<sup>12</sup> and Arndt et al.<sup>13</sup> from the early 1980s (Figs. 9–11).

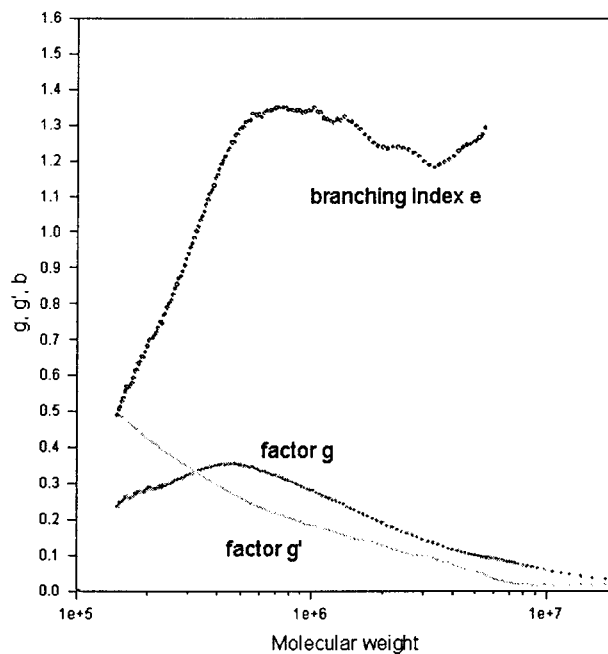
As a consequence, the structure of the resins changes with the molecular weight. At lower molecular weights, the structure can be described as treelike, while molecules of the high molecular weight region have comblike structures. In between, a gradual change of structure with increasing molecular weight is to be seen. Furthermore, suitable polymerization conditions can yield LDPEs where the periphery of molecules is much more long-chain branched than is the center of the coil. When passing into a tubular reactor zone with high temperature and high conversion, already existing LCBs shield the center of the molecule against abstraction of hydrogen by a radical and, therefore, at this stage, lead to the formation of LCBs only at the periphery of the molecules. Such structures would have increased  $R_g$  values and therefore higher  $\epsilon$  values compared

with randomly branched molecules with the same molecular weight. The reason for the tubular resins showing such differences in molecular weight distribution and LCB concentration in comparison to autoclave grades must be due to the special conditions during ethylene polymerization in the tubular reactor.

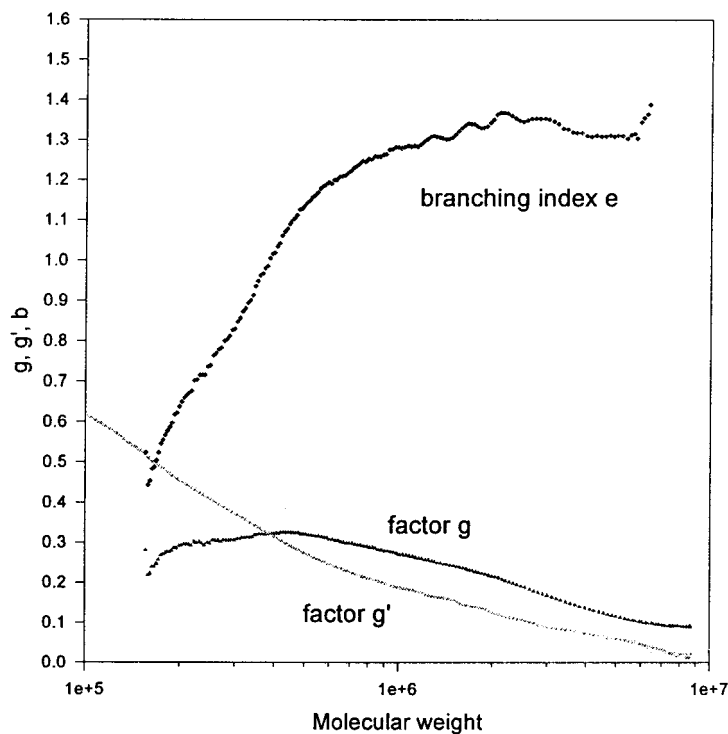
Molecular structure data of the polymers including the linear PEs are given in Table II. The results and considerations presented above cast additional light on the average molecular weights of the resins shown in Table II.

In general, the LS technique gives a higher  $M_w$  value for the branched samples having a second peak in the LSD chromatogram. Particularly striking, however, are the values of  $M_z$  obtained by SEC–LSD, which can be several times higher than are the values obtained by SEC–VD. This is a clear illustration of the increased sensitivity of SEC–LSD over the viscometer at the high molecular weight region of LDPEs. This becomes apparent in Figure 12 where the MWD of sample T2 obtained by both SEC–LSD and SEC–VD is displayed. The SEC–VD results for sample T2 suggest a much lower portion of molecules with  $M > 2 \times 10^6$  Mio.

However, as discussed earlier, the sensitivity of the VD is greater for linear polymers than for branched polymers at the very end of the mo-



**Figure 10** Molecular weight dependence of the branching indices  $g$ ,  $g'$ , and  $e$  of LDPE A1.



**Figure 11** Molecular weight dependence of the branching indices  $g$ ,  $g'$ , and  $e$  of LDPE A2.

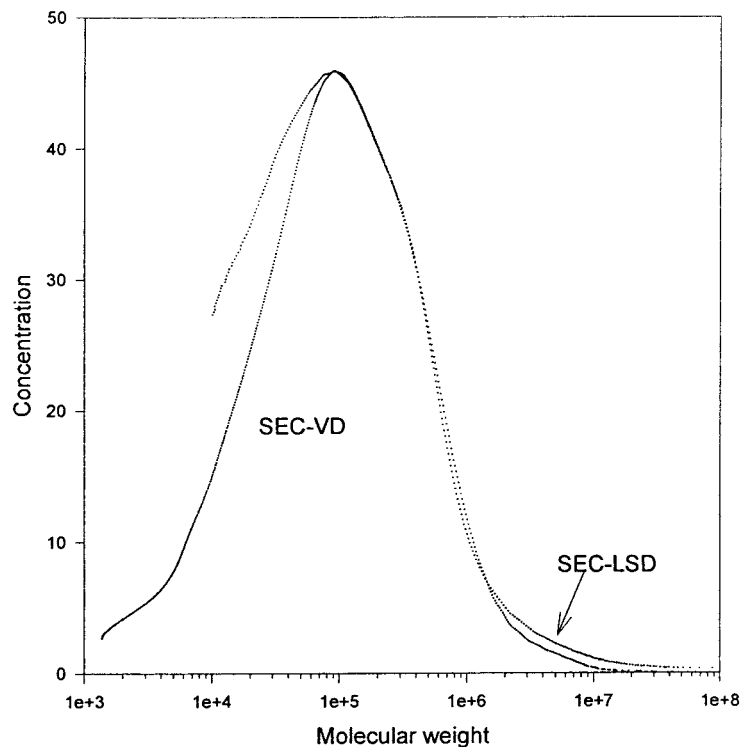
lecular weight distribution. This is particularly well illustrated for the  $M_w$  and  $M_z$  values obtained by both techniques for the linear HDPE and SRM 1475 given in Table II. The values are in very close agreement, emphasizing that both

instruments have a similar capability for analyzing high molecular weight species in linear polymers.

These results are of crucial importance for the current discussion of using a combination of

**Table II** Molecular Weight Averages and IV Data of Polymers

Polymer	Method	$MI$	$M_w$	$M_n$	$M_z$	$M_z/M_w$	IV (g/dL)
SRM 1476	SEC-LSD	1.19	117,500	23,200	3,265,000	28	—
	SEC-VD		88,600	21,000	231,300	2.6	0.91
T1	SEC-LSD	?	181,300	—	1,565,000	8.6	—
	SEC-VD		166,100	22,700	968,100	5.6	0.98
T2	SEC-LSD	10	233,200	—	1,830,000	7.8	—
	SEC-VD		175,000	18,200	672,400	3.8	1.03
A1	SEC-LSD	70	118,500	—	761,000	6.4	—
	SEC-VD		110,000	17,600	258,300	2.3	0.75
A2	SEC-LSD	10	201,800	—	679,900	3.4	—
	SEC-VD		197,800	20,500	568,000	2.9	0.91
HDPE	SEC-LSD		374,200	—	2,042,000	5.5	—
	SEC-VD		361,300	19,500	2,066,000	5.7	3.30
SRM 1475	SEC-LSD		57,200	—	151,500	2.6	—
	SEC-VD		58,800	18,700	145,900	2.5	1.01



**Figure 12** Comparison of T2 molecular weight distribution obtained by SEC-VD and SEC-LSD.

a viscometer and an LSD with SEC to determine the radius of gyration ( $R_g$ ) values. IV values derived from SEC-VD and molecular weights derived from SEC-LSD can be used in the Fox-Flory equation to yield the radius of the gyration values. The lack of sensitivity of SEC-VD for branched PEs at the very end of the molecular weight distribution questions the applicability of this approach. A detailed study of these findings will be the subject of a further article.

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