High Molecular Weight Tail and Long-Chain Branching in SRM 1476 Polyethylene

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Received 8 June 1998; accepted 25 November 1998

ABSTRACT: The composition of the high molecular weight tail in the branched polyethylene standard reference material SRM 1476 was studied in detail using size exclusion chromatography coupled with a refractive index, a viscosity, and a light scattering on-line detector. The light scattering determinations of both molecular weight and radius of gyration point at a difference in kind between the molecular species below and above 10^6 Da. In particular, above 10^6 Da, increases in molecular weight resulted in a marked "densification" process. This is consistent with a greater concentration of long-chain branching and/or with a change in molecular architecture. Previous literature results for this polymer and a critical comparison of the performance of the different detectors are also discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2807–2812, 1999

Key words: high molecular weight tail; long-chain branching; low-density polyethylene

INTRODUCTION

The standard reference material SRM 1476 is a low-density polyethylene (LDPE) that is widely used as a calibrant in chromatographic experiments. Since the original characterization by the U. S. National Bureau of Standards the polymer has been the subject of numerous investigations, which was particularly stimulated by advances in techniques. The advent of on-line $viscositv^{1-10}$ and light scattering detectors^{1,2,6,8,10-18} with size exclusion chromatography (SEC) has enabled the reporting of a great deal of data on weight-average and number-average molecular weights (M_w) and M_n). However, these investigations have not yielded an altogether consistent picture of the molecular weight distribution of SRM 1476, largely because this polymer exhibits a complex

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Journal of Applied Polymer Science, Vol. 73, 2807-2812 (1999)

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composition that is due to the combined presence of a high molecular weight tail^{6,7,10,18–20} and longchain branching.^{3–6,9–12} In this context, the work by de Groot and Hamre is of particular note.¹³ Their systematic study, using SEC and low-angle laser light scattering, conclusively established the high molecular weight component's susceptibility to shear degradation.

Prompted by the availability of state of the art facilities, we carried out a fresh appraisal of SRM 1476. By coupling a light scattering detector and a viscosity detector to the size exclusion chromatograph, some unique structural features of the high molecular weight region were revealed.

EXPERIMENTAL

Instrumentation

The size exclusion chromatograph used in this study consisted of a Waters Associates 150CV equipped with a Waters differential refractometer (DRI), a two angle (15 and 90°) Precision Detector PD2040 laser light scattering detector (LSD), and a Viscotek model 150R differential bridge viscometer detector (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⁻¹ at 140°C and trichlorobenzene as the eluant. A 5- μ m on-line filter was connected in front of the columns. The 10- μ L flowthrough cell of the LSD was positioned immediately after the columns. The DRI and VD were connected in parallel behind the LSD. The flow was split approximately 50 : 50 between the DRI and VD lines. An injection volume of 400 μ L was employed throughout. The columns were calibrated using 22 polystyrene (PS) standards supplied by Polymer Laboratories with molecular weights (*M*) ranging from 2,050 to 4,000,000.

Data handling was accomplished using the Viscotek TriSEC and Precision Detectors software packages. Ascii files were used to transfer raw data from both software packages so the date could be processed using Microsoft Excel and Sigma Plot (Jandel Scientific).

The software automatically compensated for the interdetector volume by appropriately shifting the signal from the VD or the LSD for superimposition on the peak from the DRI signal. The extent of the shift was determined using a narrow standard. In our case a polystyrene standard with a peak molecular weight of 65,000 Da and a polydispersity of 1.06 was used.

Performance of the VD was checked by measuring the Mark–Houwink coefficients for PS, which were derived from the 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 literature.²¹ The LSD instrument constants were calibrated using a PS standard with a peak molecular weight of 65,000. The performance was then assessed by measuring the molecular weights of 22 PS standards. The values were found to agree to better than 5% with the quoted values from Polymer Laboratories.

Sample Preparation

For comparison with SRM 1476, an ethylene homopolymer, high-density PE (HDPE, M_w 370,000, BP Chemicals), was employed.

All solutions were prepared in filtered 1,2,4-trichlorobenzene containing 0.1 wt % of antioxi-

dant (Santonex 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 ~ 20 mg of polymer in 20 mL of 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 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

The response from the three detectors (raw data) for SRM 1476 is shown in Figure 1. The retention volumes are corrected for the interdetector volumes.

The LSD chromatogram for the 15° angle exhibits a sharp second peak at very small elution volumes (<26 mL). The chromatogram for the 90° angle (not shown) was very similar, but it showed slightly lower sensitivity at higher molecular weights. The detection of a second peak at small elution volumes is consistent with earlier reports.^{6,10,18,20}

This secondary peak was not present in the response of the DRI and VD detectors, which is consistent with earlier on-line viscometer and SEC studies.^{3-7,9,10}

The difference in response between the LSD and the VD detectors is not surprising because it reflects the difference in sensitivity. The LSD signal is proportional to cM (c, concentration; M, molecular weight), while the VD response is proportional to cM^{α} where α is the Mark–Houwink parameter. For unbranched PE, α is ~0.7. However, for the high molecular weight fraction of SRM 1476 α approaches 0.1, resulting in a much reduced response. The DRI responds according to $c.^2$

A more informative plot of M as a function of retention volume is shown in Figure 2. This was derived from the raw data in Figure 1. In the case of the viscometry results, the universal calibration approach was used to calculate the value of M. The LSD results for the HDPE are also shown in this figure for comparative purposes.

Because of the sensitivity considerations discussed above, the range over which reliable data can be obtained depends upon the detector type and polymer molecular weight distribution. The limits of the measurement are defined by the onset of an unacceptable level of noise. From the

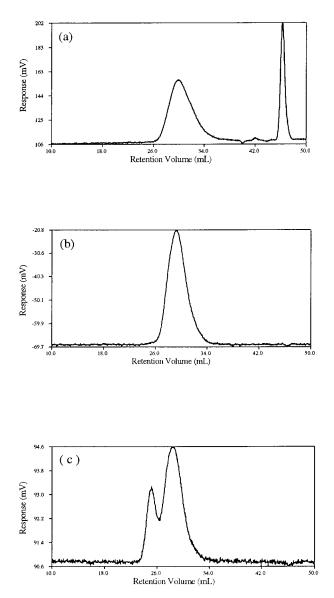


Figure 1 Chromatographs for SRM 1476 obtained by (a) a refractive index, (b) viscometer, and (c) a light scattering detector.

data in Figure 2 the cutoffs for the LSD response were chosen to be at retention values of 26.03 and 32.40 mL. The corresponding cutoffs for the VD response were chosen as 26.48 and 34.01 mL. Over the range where direct comparison is possible, there is good agreement between the LSD and VD data. More significantly, however, a clear change in slope is detected in the LSD results below a retention volume of 27.2 mL. In this region a sharp rise in molecular weight is measured and values up to 1.5×10^6 Da are detected.

This change in slope of the LSD plot is indicative of a different kinds of molecular populations above and below the 26-mL retention volume.

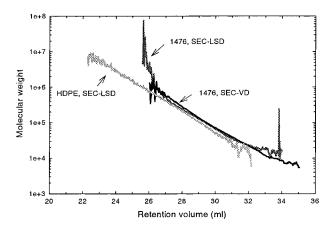


Figure 2 Molecular weight versus retention volume for SRM 1476 and a linear HDPE.

We submit that below this critical retention volume the higher than expected molecular weights are due to the presence of long-chain branching. In this fraction of the polymer the lower retention volume fraction has not only a higher molecular weight but it also has a higher concentration of long-chain branches (LCBs).

Conventional representations of the molecular weight distribution of SRM 1476 obtained by SEC-VD and SEC-LSD are shown in Figure 3. For consistency, here the curves are truncated in line with the cutoffs identified in Figure 2. Over most of the range the distributions are quite similar. The higher sensitivity of the LSD, results in a small tail with M in excess of 10⁶ Da. Clearly, in order to calculate the molecular weight averages one needs to rely on an extrapolation. In our case

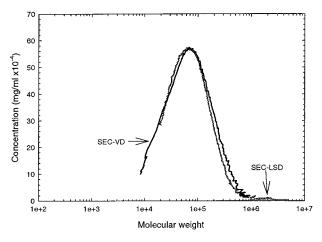


Figure 3 Molecular weight distribution of SRM 1476 obtained using a light scattering detector and a viscosity detector.

| Method | M_w | ${M}_n$ | M_z | M_w/M_n | IV (g/dL) | Ref |
|----------------------|---------|---------|------------|-----------|-----------|-----|
| This study | | | | | | |
| SEC-LSD ^a | 108,300 | 21,000 | 1,029,000 | 5.2 | _ | |
| SEC-VD | 86,300 | 21,000 | 204,000 | 4.1 | 0.91 | |
| Literature values | | · | | | | |
| SEC-LALLS | 100,300 | 38,400 | 1,536,200 | 2.6 | _ | 6 |
| SEC-LALLS | 126,500 | 39,600 | 1,091,500 | 3.2 | — | 10 |
| SEC-LALLS | 103,200 | 26,200 | 3,336,000 | 3.9 | _ | 12 |
| SEC-LALLS | 76,100 | 21,800 | _ | 3.5 | _ | 14 |
| SEC-LALLS | 92,400 | 27,900 | 3,388,000 | 3.3 | _ | 17 |
| SEC-LALLS | 100,400 | 28,000 | >3,000,000 | 3.6 | _ | 18 |
| SEC-VD | 98,100 | 25,400 | 237,000 | 4.0 | 0.91 | 3 |
| SEC-VD | 84,100 | 17,900 | | 4.7 | _ | 4 |
| SEC-VD | 88,200 | 23,000 | _ | 3.8 | — | 5 |
| SEC-VD | 101,500 | 40,100 | 278,100 | 2.5 | 0.97 | 6 |
| SEC-VD | 85,500 | 28,000 | 312,500 | 3.1 | _ | 7 |
| SEC-VD | 81,300 | 25,770 | 234,300 | 3.2 | 0.93 | 9 |
| SEC-VD | 116,400 | 32,900 | 796,600 | 3.5 | _ | 10 |
| LALLS off-line | 221,000 | | _ | — | — | 18 |
| LALLS off-line | 215,000 | _ | | _ | _ | 19 |
| LALLS off-line | 140,000 | _ | | _ | _ | 22 |
| Viscometry off-line | 96,500 | 22,700 | | 4.3 | 0.94 | |
| Viscometry off-line | 90,700 | 19,500 | _ | 4.7 | 0.90 | 22 |
| Viscometry off-line | 84,700 | 21,900 | _ | 3.9 | 0.85 | 23 |
| Certificate value | , | , | | | 0.90 | 24 |

Table I Molecular Weight Averages and Intrinsic Viscosity Data (IV) of SRM 1476

LALLS, low angle laser light scattering.

^a Average of five measurements.

TriSEC (Viscotek) software and Precision Detector software were used for the SEC-VD and SEC-LSD, respectively. The values and other literature data are shown in Table I. In view of the sensitivity limits of the different detectors, of the uncertainties in the extrapolation procedure, of the differences in experimental conditions (e.g., flow rate, columns), and of the complex nature of the high molecular weight tail of SRM 1476, it is not be surprising that a wide variation of molecular weight averages has been reported, depending on the technique employed.

In general, the techniques employing light scattering give a higher M_w value. Particularly striking, however, are the values of z-average molecular weight (M_z) obtained by SEC-LSD, which can be up to an order of magnitude higher than the value obtained by SEC-VD.^{12,17,18} It was these differences in molecular weight averages that first led some authors^{6,7,10,18,19} to suggest the presence of a high molecular weight tail in the polymer.

MacRury and McConnell attributed the LSD response of SRM 1476 and the very large M_z

observed, to the presence of small amounts of microgel.¹⁸ Grinshpun et al. described the 3.4 \times 10⁶ value of M_z that they observed as arising from spikes in their LS chromatogram and attributed them to supermolecular aggregates.¹⁷ Because no spikes were observed in the light scattering chromatogram in Figure 1, the presence of undissolved aggregates can be ruled out in our work.

To gain further insight into the structure of SRM 1476, the radius of gyration was determined as a function of molecular weight (measured using the LSD) and the results were compared with those for the unbranched HDPE sample. The plots are shown in Figure 4. Two features are noteworthy.

First, for $2 \times 10^5 < M < 10^6$, the radius of gyration (r_g) of SRM 1476 is lower than the one for the unbranched HDPE, which is consistent with the presence of LCBs, although the r_g increases at a similar rate as a function of molecular weight. Second, for $M > 10^6$, the radius of gyration of SRM 1476 reaches a plateau value

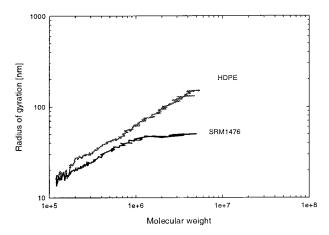


Figure 4 Radius of gyration versus molecular weight for the two polymers studied.

 ~ 52 nm. In the same region, the equivalent unbranched polymer gives a $r_g > 100$ nm.

Although it is premature to draw a definitive conclusion, the data point to the presence of two distinctly different molecular populations. In fact, the characteristics of the population with $M > 10^6$ are so peculiar that it seems reasonable in this case to invoke a different molecular architecture, as well as an increasing number of LCBs per molecule. The above results and considerations cast additional light on and add an extra dimension to the data presented in Figure 2.

The conventional presentation of LCB distribution data involves the ratio g' of the intrinsic viscosities of the branched polymer and the unbranched polymer of equivalent molecular weight. For completeness and comparative purposes, this plot is shown in Figure 5. Also included is a plot of g versus M, where g is the ratio of the mean square radius of gyration for the branched and unbranched species. The two curves span different molecular weight ranges, which is consistent with the considerations on the sensitivity limits of the two detectors. The fact that g approaches zero at high molecular weights confirms that these molecules have a compact sphere geometry.

As a final comment, it should be pointed out that the secondary peak observed in the light scattering signal of SRM 1476 is not unique: it was also observed in some commercial LDPEs, implying that LDPEs can exist with a marked molecular heterogeneity in the high molecular weight tail. This will be the subject of a another study.

CONCLUSIONS

The present study highlights the composite nature of the high molecular tail of SRM 1476. Although there is evidence of branching across the whole molecular weight distribution, the region above 10^6 Da appears rather special. Light scattering measurements indicate the presence of marked densification. This can be rationalized in terms of a particular combination of LCB concentration effects and molecular architecture. The population $M > 10^6$ is different in kind from that at $M < 10^6$. These findings explain the discrepancies observed in the molecular weight averages of SRM 1476 reported in the literature, in particular M_z .

All the results discussed in this article were obtained using a flow rate of 1 mL/min. In light of the findings by de Groot and Hamre,¹³ it is fitting to comment on the effect of shear degradation. These authors showed that by decreasing the flow rate, the separation and relative height of the two peaks in the chromatograms change. However, the general shape of the profile does not change. We therefore regard the present conclusions as having general validity. Any shear degradation (related to operating conditions) would merely alter the relative concentration of the structurally different molecular species. Indeed, work currently in progress in this laboratory (to be published shortly) fully supports this statement. It will also be shown that the observation of a high molecular weight species in SRM 1476 is not unique to this material but is observed in other LDPEs.

Dr. F. Beer gratefully acknowledges BP Chemicals' support in the form of a CTO Research Fellowship. The

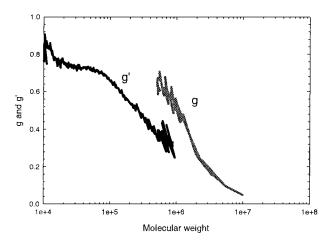


Figure 5 Molecular weight dependence of the branching indices g and g' for SRM 1476.

authors wish to thank BP Chemicals for granting permission to publish this work.

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