

On the Accuracy of SEC Analyses of Molecular Weight Distributions of Polyethylenes

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Synopsis

Molecular weights of National Bureau of Standards SRM 1476 polyethylene have been reported by six laboratories. The measured values are in remarkably good agreement and all show that \bar{M}_w from SEC/LALLS analyses is significantly lower than the same average determined by LALLS on the whole polymer itself. This is shown to be due to the presence of high molecular weight species which become too diluted on passage through the SEC columns to be observed in the LALLS detector. The resulting error in \bar{M}_w and higher averages may vary from slight to very serious, depending on the molecular weight distribution of the particular polyethylene. A procedure is described to detect the presence of such high molecular weight species.

INTRODUCTION

There have been a number of recent reports on molecular weight averages of National Bureau of Standards 1476 standard reference material branched polyethylene.¹⁻⁵ This polymer is stated³ to be a low conversion tubular reactor product with density 0.931 g·cm⁻³ and melt index⁶ 1.2 dg/min. The published data are listed in Table I along with results of our own measurements.

All results are in good agreement and all show that \bar{M}_w measured by SEC is significantly lower than the same average from light scattering analyses of solutions of the whole polymer. It has been suggested⁵ that high molecular weight species may be trapped in the SEC column packing. There is some support for this hypothesis in studies of the effects of different filter media on molecular weight averages from SEC.²

If this suggestion were indeed correct, it would mean that polyethylene molecules would be building up on the columns during successive analyses. Since column clogging is not a serious problem with this polymer, it must follow that trapped species from prior experiments are being released during succeeding analyses. This would invalidate the use of SEC for analyses of this polymer.

The work reported here was intended to examine the reasons for discrepancies between SEC and light scattering measurements of \bar{M}_w of some polyethylenes and, so doing, to assess the accuracy of the SEC method. Most attention was paid to the NBS 1476 polyethylene since data from other workers are also available for this polymer. Other polyethylenes were also included in this study, however, and the conclusions are generally applicable.

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EXPERIMENTAL

All light scattering measurements were performed with a KMX-6 (Chromatix Inc., Sunnyvale, Calif.) low angle laser light scattering (LALLS) photometer using the high temperature sample cell supplied with this instrument. Measurements were made at $6-7^\circ$ to the incident beam. Negligible angular dependence of scattering intensity was detected with this instrument in the $3-7^\circ$ useful range available. The photometer incorporates a He-Ne laser source ($\lambda = 6328 \text{ \AA}$). The specific refractive index increment (dn/dc) was also measured at the same wavelength, with a Chromatix differential refractometer. Both measurements were made at 145°C . The measured dn/dc was -0.098 mL/g . MacRury and McConnell⁵ report $-0.091 \pm 0.002 \text{ mL/g}$ for NBS 1476 in trichlorobenzene (TCB) at 135°C and the same wavelength. Sample solutions had concentrations of 1–3.5 mg/mL.

All measurements were made in TCB solutions. This is a relatively good solvent for polyethylene. Because the crystal melting point of polyethylene is near 140°C , this polymer tends to form supermolecular aggregates even at 145°C in TCB. These structures can be eliminated by heating solutions to 160°C for 1 h before cooling to 145°C for molecular weight measurements.⁷ The absence of aggregates is shown in separate light scattering experiments by the agreement of second virial coefficients with values estimated for the \bar{M}_w indicated⁸ and by the drastic reduction in large particle "spikes" in light scattering intensity.

All solutions contained 0.1% (w/v) 4,4'-thiobis(3-methyl-6-*tert*-butyl phenol) antioxidant.

SEC measurements were made with a Waters 150C liquid chromatograph equipped with 500, 10^4 , and 10^5 \AA ultrastyrigel columns. A solvent flow rate of 0.5 mL/min was found to give good resolution. In some experiments DuPont Zorbax columns SE-60, -1000, and -4000 were used in series at a flow rate of 1.0 mL/min. Polymer samples were injected with concentrations of 3.5–5.5 mg/mL. The polymer concentration in the eluant was monitored with the Waters differential refractive index and the Chromatix low angle laser light scattering detectors. All solutions were filtered through a $0.5 \mu\text{m}$ polytetrafluoroethylene filter (FHUP, Millipore Corp.) before analysis.

Light scattering measurement on the whole polymer were made by removing the columns from the size exclusion chromatograph and employing only the pump, heater and automatic injector of this unit. Samples of polyethylene solutions at 1.0–3.5 mg/mL were injected into the SEC unit at 145°C and their turbidities were measured as they flowed through the KMX-6 light scattering photometer, also at 145°C .

RESULTS AND DISCUSSION

Figure 1 shows the SEC chromatograms of SRM 1476 on Waters Ultrastyrigel columns. This polymer is clearly bimodal. The chromatograms obtained on du Pont silanized porous silica columns are shown in Figure 2. Molecular weight averages calculated from analyses with the different columns agree closely, as shown in Table I. These values also agree with results obtained by others using Shodex polystyrene gel columns.⁵ There is clearly no significant effect of column material on the experimental results.

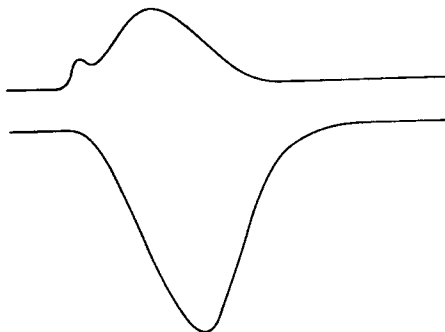


Fig. 1. SEC traces of NBS 1476 polyethylene in TCB at 145°C. The chromatogram was obtained with porous polystyrene gel packings. The upper trace is from the LALLS detector and the lower trace from the differential refractometer. The LALLS is first in the series.

The \bar{M}_w value of Wild and co-workers³ is somewhat lower than our value. This is probably because these workers used a differential refractometer detector which is not as sensitive to the higher molecular species as the LALLS detector. An entry in Table I gives averages obtained in our study using only the differential refractometer and a universal calibration based on polystyrene hydrodynamic volumes.^{9,10} The values measured are lower than with LALLS detection and are in reasonable agreement with those of Wild and co-workers,³ who used a calibration based on linear polyethylene fractions.

The molecular weight averages reported by Axelson and Knapp¹ are also lower than our results. Two reasons may be suggested to account for this difference. In the first place, while the solvent used by these workers, 1-chloronaphthalene, provides a favorable specific refractive index increment for polyethylene solutions

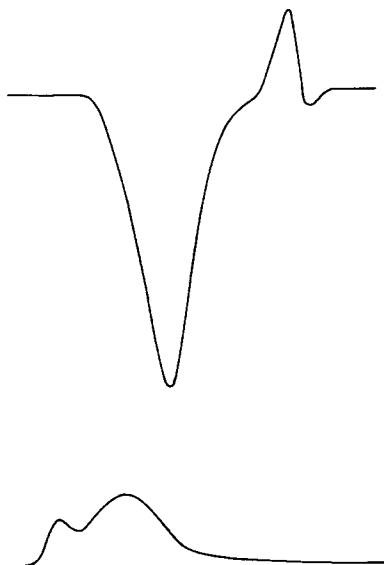


Fig. 2. SEC traces of NBS 1476 polyethylene using porous silica column packings. The lower trace is the LALLS signal in this case.

TABLE I
 Molecular Weight Averages of SRM 1476 Polyethylene

| Reference | Size exclusion chromatography | | | | Light scattering |
|--------------------------|-------------------------------|-------------|------------------|-----------------------|--|
| | \bar{M}_n | \bar{M}_w | \bar{M}_z | \bar{M}_w/\bar{M}_n | analyses of whole polymer \bar{M}_w |
| 1 ^a | 21,800 | 76,000 | — | 3.49 | — |
| 2 | 20,100 | 90,900 | — | 4.52 | — |
| 3 | 21,900 | 84,700 | — | 3.91 | — |
| 4 | — | — | — | — | 216,000 |
| 5 | 28,000 | 100,400 | $>3 \times 10^6$ | 3.59 | 221,000 \pm 9,000 |
| This work ^b | 28,400 | 93,100 | 3,722,000 | 3.28 | 214,000 |
| This work ^c | 31,300 | 98,100 | 3,867,000 | 3.13 | — |
| This work ^{b,d} | 27,500 | 74,200 | 160,000 | 2.70 | — |

^a Measurements in 1-chloronaphthalene at 150°C.

^b Measurements with Waters Ultrastaygel columns (500, 10⁴, and 10⁵ Å in series).

^c Measurements with DuPont Zorbax columns (SE-60, SE-1000, and SE-4000 in series).

^d Measurements using differential refractive index detector and calibration based on polystyrene hydrodynamic volumes.^{9,10}

it is not a strong solvent for this polymer. Supermolecular aggregates will persist in solution even at 150°C.⁷ These will be filtered out by the column packing or appear in the LALLS response as "spikes" on the detector trace. Such large species will effectively not be counted in the analysis of molecular weight distribution. Secondly, an unusually high polymer concentration was used in the cited work. This may produce distortions of the high molecular weight tail of the SEC chromatogram and shift measured molecular weight averages to lower values.¹¹ (This is a probable cause of many of the failures of preparative SEC to produce sharp fractions.)

With these explanations, it can be seen that the measured molecular weight averages measured in this work are in good agreement with those of earlier workers. The coincidence of data is in fact remarkably close, for this type of analysis.

The data in Table I also show conclusively that light scattering measurements on this whole polymer produce an \bar{M}_w , which is more than double the value obtained by careful SEC analyses of the same material.

In order to investigate the cause of this discrepancy, we have collected the effluents from SEC analysis of NBS 1476 polyethylene and sample C (a linear low density polyethylene with melt index 1.0 g/10 min and 0.920 density). These solutions were concentrated by evaporating most of the solvent and their weight average molecular weights were measured by LALLS. The results are shown in Table II. These data show that there may be some loss of high molecular weight species in the SEC columns, as suggested by MacRury and McConnell.⁵

An alternative explanation could be molecular degradation during passage through the SEC apparatus.¹²⁻¹⁴ Although this effect cannot be entirely ruled out, it is not likely to be very significant in this case. The flow rate in the Ultrastaygel columns was low (0.5 mL/min), tending to minimize shear degradation. The flow rate in the Zorbax porous silica columns was 1.0 mL/min, but the resulting higher pressure drop did not cause any decrease in measured molecular weight averages (Table I).

TABLE II
Effect of Passage through SEC Columns on \bar{M}_w from LALLS Measurements

| Sample | \bar{M}_w from LALLS on original polymer | \bar{M}_w from SEC analysis with LALLS detector | \bar{M}_w from LALLS on collected effluent from SEC analysis |
|----------|--|---|--|
| NBS 1476 | 214,000 | 93,100 | 167,800 |
| LLDPE C | 217,400 | 185,300 | 200,100 |

Neither column plugging nor shear degradation appears to be the major reason for the observed discrepancies between SEC and light scattering measurements of \bar{M}_w . This is clearly shown by the fact that the \bar{M}_w of the polymer in the solution which passed through the columns is higher than the value measured during the actual analysis in these columns. We are left with the disturbing conclusion that \bar{M}_w (and possibly higher averages) measured by SEC may be in error and that this error may vary from slight, as in sample C, to serious as in NBS 1476.

We now suggest a likely reason for this deficiency in SEC measurements and a procedure to detect its occurrence.

The parameter used to summarize light scattering data is the reduced scattering intensity R_θ , which is defined for unit volume of scattering solution as:

$$R_\theta = \frac{I'_\theta r^2}{I_0(1 + \cos^2\theta)} = \frac{2\pi^2 n_0^2 (dn/dc)^2 c}{\lambda^4 L (\bar{M}_w^{-1} + 2A_2 c)} = \frac{K c \bar{M}_w}{1 + 2A_2 c \bar{M}_w} \quad (1)$$

Here I'_θ is the intensity of light scattered at a distance r from the scattering volume and angle θ to the incident beam of intensity I_0 . Also n_0 and n are the respective refractive indices of the solvent and solution with concentration c ($\text{g}\cdot\text{cm}^{-3}$), dn/dc is the specific refractive index increment of the solution ($\text{cm}^3\cdot\text{g}^{-1}$), λ is the wavelength of incident light (cm), L is Avogadro's number, and K ($\text{mol}\cdot\text{g}^{-1}\cdot\text{cm}^{-1}$) is an optical constant defined by terms in eq. (1).

To obtain a detectable signal with the LALLS photomultiplier, R_θ should be $>10^{-7} \text{ cm}^{-1}$ per unit volume of the cell. Given the apparatus and solutions used in this work, K is typically $10^{-7} \text{ mol}\cdot\text{g}\cdot\text{cm}^{-1}$. Therefore, a necessary condition for satisfactory use of LALLS is

$$\frac{R_\theta}{K} = \frac{c \bar{M}_w}{1 + 2A_2 c \bar{M}_w} > 1 \quad (\text{g}\cdot\text{cm}^{-3}\cdot\text{mol}^{-1}) \quad (2)$$

To consider our problem, we assume reasonable values⁸ for A_2 to be $10^{-3} \text{ cm}^3\cdot\text{mol}\cdot\text{g}^{-1}$ for a polyethylene of $\bar{M}_w = 10^3$ and $A_2 = 10^{-4}$ for \bar{M}_w of 10^6 . Under SEC conditions, the second term in the denominator of eqs. (1) and (2) is negligible, and we may rewrite the condition of eq. (2) as

$$c \bar{M}_w > 1 \quad (3)$$

Equation (3) suggests that low molecular weight polyethylene would be "invisible" to LALLS at concentrations as high as 10^{-3} g/mL , while high molecular weight material can be readily detected at concentrations as low as 10^{-5} or 10^{-6} g/mL .

When the polymer sample is analyzed by SEC, it is diluted in the columns and the concentration of large species may become too low (e.g., about 10^{-7} g/mL)

to be detected by the LALLS or DRI detectors. Large molecules which can be detected in LALLS analysis of the whole polymer will not be seen if they are diluted during passage through the SEC columns and \bar{M}_w measured by SEC/LALLS is therefore lower than that from LALLS alone on the whole polymer sample.

Increasing the concentration of the samples injected into the SEC apparatus is not a universal solution to this problem because higher concentrations may cause overlap of species with different molecular weights, at the high molecular weight end of the chromatogram.¹¹

With the apparatus available at present, the best procedure appears to be to measure \bar{M}_w by LALLS alone as well as to analyze the molecular weight distribution by SEC. If the \bar{M}_w values obtained by the two measurements do not agree, this is an indication that high molecular weight species may be undetected in the SEC analysis. Table III lists a number of such comparisons for different polyethylenes. It is clear that the error in \bar{M}_w and higher averages from SEC may vary from slight to very serious. The procedure recommended reveals the presence of high molecular weight species, even though their concentrations may be too low to be taken into account in the computed molecular weight averages.

It might be expected that the problem cited here would be most serious in general with high-pressure-process low-density polyethylenes because these materials may have particularly broad molecular weight distributions. These are also the polyethylenes that are characterized by long chain branching. Hamielec and co-workers¹⁵ have pointed out that the molecular weight distribution obtained by the SEC/LALLS technique is not correct for polymers with long branching. They have recommended that such data be used only to calculate \bar{M}_w , for the sake of accuracy. The work reported here shows that \bar{M}_w may also be suspect, if the polymer comprises low concentrations of very high molecular weight polyethylenes.

It is possible that the problem identified in this article can be solved by use of a programmable device to vary the sensitivity of the LALLS photomultiplier detector as needed to register the turbidities of all the eluting solutions. Such a device has been mentioned in the literature¹⁵ and is being tested in our laboratory for this purpose.

The work reported here shows that use of a differential refractometer detector

TABLE III
Comparison of SEC and LALLS Measurements of \bar{M}_w of Polyethylenes

| Sample | SEC/LALLS | | | LALLS | Type |
|----------|-------------|-------------|-------------|-------------|-------|
| | \bar{M}_n | \bar{M}_w | \bar{M}_z | \bar{M}_w | |
| NBS 1476 | 28,400 | 93,100 | 3,722,000 | 214,000 | LDPE |
| D | 43,200 | 176,300 | 1,519,000 | 189,000 | LDPE |
| E | 21,800 | 96,000 | 686,500 | 115,000 | LDPE |
| F | 18,350 | 151,600 | 719,000 | 167,000 | LDPE |
| G | 28,300 | 233,000 | 1,312,000 | 251,000 | LDPE |
| H | 38,000 | 145,300 | 700,000 | 161,200 | LDPE |
| I | 17,200 | 45,900 | 225,900 | 58,100 | LDPE |
| C | 46,400 | 185,300 | 606,700 | 217,400 | LLDPE |
| A | 46,000 | 144,000 | 406,000 | 233,600 | HDPE |
| B | 60,400 | 144,500 | 372,000 | 208,300 | LDPE |

alone is inadequate for SEC analyses of polyethylene. A LALLS detector should also be employed to reveal the high molecular weight portion of the distribution.

Support of this research by the Natural Sciences and Engineering Research Council of Canada is appreciated. The authors are grateful to A. C. Ouano for helpful discussions.

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Received May 17, 1983

Accepted August 23, 1983