

Characterization of high-molecular-mass polyethylenes by gel permeation chromatography–low-angle laser-light scattering

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ABSTRACT

Gel permeation chromatography–low-angle laser-light scattering (GPC–LALLS) has been applied to the analysis of high-molecular-mass polyolefins. It was found that changing the particle size of the column packing from 10 to approximately 50 μm resulted in an increase in the molecular mass of NBS 1476 of from 100 000 to 195 000. It was also found that changing the flow-rate from 1.0 to 0.1 ml/min resulted in an increase in the molecular mass of the same sample of from 195 000 to 280 000 for the large particle size gel columns. Increases were also seen with commercial low-density samples when changing these same conditions, but the increases were not as large in magnitude. A change in the frit size on the columns did not seem to have an effect on the measured molecular masses of the NBS 1476 samples. Another finding in this study was that slurry high-density polyethylene samples which previously had been very difficult to characterize using GPC–LALLS gave much higher molecular masses which were much more reproducible when characterized using the large particle size columns with low flow-rates.

INTRODUCTION

Since its development as a practical technique [1–3], classical wide-angle light scattering has proven to be a very powerful tool for the polymer chemist studying polyethylene. The technique can give absolute mass-average molecular masses, second virial coefficients and radii of gyration of dissolved polyethylene in solution [4,5]. Its main limitation is its difficulty of use and the fact that it does not give any information on the polydispersity of the sample. Conversely, gel permeation chromatography (GPC) is generally much easier to use and gives an approximation of all the molecular mass averages [6,7]. The disadvantages of this technique are that it requires calibration and it is capable of only giving an apparent molecular mass for poly-

ethylenes with long chain branching, *i.e.*, low-density polyethylenes. In theory then, the combination of these two polymer characterization tools should result in a very powerful technique which should give *z*-average, mass-average, and number average molecular masses without calibration. With the advent of a low-angle laser-light scattering instrument (LALLS) it is now possible to combine the two techniques [8–11] and this has been applied to the analysis of polyolefins [12–14]. It has also been reported that the combination of these two characterization methods can be used to determine the level of long chain branching in low-density polyethylenes [15–17].

We have observed many difficulties over the last few years in our attempts to characterize the molecular mass of higher-molecular-mass polyethylene resins using GPC–LALLS. These include poor reproducibility of both the LALLS and the differential refractive index (DRI) detec-

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tor responses, spiking in the LALLS detector response, partial plugging represented by increases in the pressure transducer response, and lack of correlation with rheological data. All of these results seem to suggest that the polymer is having difficulty passing through the GPC column due to resistance in the frits, in the gel itself, or perhaps in the post-column filter. Another example of the difficulty in characterizing high-molecular-mass polyethylene can be found in the literature on National Bureau of Standards (NBS) 1476 polyethylene standard. The value obtained typically for the mass-average molecular mass using static light scattering has been around 215 000 g/mol [4,12,13], but the value obtained with GPC–LALLS is generally reported to be around 100 000 g/mol [12,13]. There are currently three theories in the literature which attempt to explain this phenomenon. One states that there is a small amount of high-molecular-mass polymer in NBS 1476 which is filtered out [4,12]. A second theory states that the small amount of high-molecular-mass polymer in NBS 1476 is diluted to such an extent that it is undetectable by the LALLS detector [13]. The third theory states that there is shear degradation during the GPC experiment [13]. Indeed, there are several references in the literature concerning shear degradation during the GPC experiment [18–21], one of which involves shear degradation of polyolefins [22].

In an effort to determine the exact cause of these difficulties in characterizing high-molecular-mass polyethylenes a detailed program was begun to evaluate GPC columns with different frit sizes and particle sizes. This report was written to discuss the initial findings of this study.

MATERIALS AND METHODS

The LALLS measurements were made using a Chromatix Model KMX-6 low-angle laser-light scattering instrument. This instrument incorporates a He–Ne laser source with a wavelength of 632.8 nm. The GPC system used was the Waters Model 150-C GPC/ALC. Molecular masses were calculated using laboratory-written software. The mass average molecular masses reported were

TABLE I
DESCRIPTION OF THE RESINS USED IN THIS STUDY

Resin	MI ^a	Density	Description
NBS 1475	2.07	0.9784	High-density polyethylene
NBS 1476	1.19	0.9312	Low-density polyethylene
LDPE-A	8.0	0.916	Low-density polyethylene
LDPE-B	4.2	0.924	Low-density polyethylene
LLDPE-A	1.0	0.92	Linear low-density polyethylene
HMW-HDPE	0.2	0.965	High-molecular-mass high-density polyethylene

^a Melt indices were determined using the standard ASTM melt index test [24].

determined using the method proposed first by Martin [23].

The solutions for study by GPC–LALLS were prepared by dissolving the samples in 1,2,4-trichlorobenzene (TCB) for at least 3 h at 160°C. All samples were prepared on a mass-to-mass basis using 1.304 g/ml for the density of TCB at 145°C. Butylated hydroxytoluene was used as a free radical scavenger and its concentration was 250 ppm (w/w).

The samples used are listed in Table I. Three sets of GPC columns were donated by Polymer Labs., one set was donated by Waters, and one set was purchased from Phenomenex. All column sets consisted of three columns. The exclusion limit of all the columns tested was approximately molecular mass $10 \cdot 10^6$ using polystyrene. These columns are described in more detail in Table II.

DISCUSSION

One of the first big challenges in characterizing polyethylenes by GPC–LALLS is to get from the point where the LALLS detector response has very few spikes. There are several keys to getting to this point. First, the column set being used must not be shedding particles. It helps tremendously to have a 0.5- μ m filter in place after the column set to aid in this. However, often this is not enough and a new column set must be

TABLE II
DESCRIPTION OF GPC COLUMNS USED IN THIS STUDY

Column manufacturer	Particle size (μm)	Column type	Frit size (μm)
Polymer Labs. ^a	10	Mixed bed	3
Polymer Labs. ^a	20	Mixed bed	5
Polymer Labs. ^a	20	Mixed bed	10
Phenomenex ^b	20	Individual pore sizes 10 ⁶ , 10 ⁵ , 10 ⁴ Å	10
Waters' Styragel ^c	30–60	Individual pore sizes 10 ⁵ , 10 ⁶ Å	10

^a Three columns 300 × 7.5 mm in size.

^b Three columns 300 × 7.8 mm in size.

^c Three columns 300 × 7.8 mm in size.

“bled” of particles for several weeks. (The length of time seems to be related to particle size with the larger particle size gel taking less time). Second, there must not be any cold spots in the system which can cause polymer to crystallize. Finally, the sample must be completely dissolved. These steps are somewhat different than those necessary to obtain good static light scattering data. This requires well filtered solutions and extremely clean glassware. In GPC–LALLS it appears that the columns themselves act as a very efficient filtration system and alleviate the necessity of cleaning glassware and often even filtering the samples.

Another big challenge in characterizing polyethylene is data interpretation. The LALLS detector often detects small amounts of polymer, sometimes referred to as microgel, which is not detected by the DRI detector. This is because the LALLS detector response is proportional to both the mass-average molecular mass and the concentration, whereas the DRI detector response is only proportional to the concentration. An example of this is shown in Fig. 1. Here one can see that there is a small amount of polyethylene which is not “seen” by the DRI detector, but gives a very strong response from the LALLS photomultiplier tube. This indicates that the polymer is very low in concentration, but very high in molecular mass. If one were to use the standard calculations to calculate the molecular mass of this sample, *i.e.*, see eqn. 1 below, the mass-average molecular mass would be

under predicted because the DRI detector response has returned to baseline where there is still a LALLS detector response.

$$\frac{Kc_i}{R_{\theta i}} = \frac{1}{M_{wi}} + 2A_{2i}c_i \quad (1)$$

In equation 1 above, K is the optical constant defined in eqn. 2 below, c_i is the concentration at each elution volume, $R_{\theta i}$ is Rayleigh's ratio at each elution volume, M_{wi} is the mass-average molecular mass of the sample at each elution volume, and A_{2i} is the second virial coefficient at each elution volume.

$$K = \frac{2\pi^2 n^2}{\lambda^4 N_A} \cdot \left(\frac{dn}{dc}\right)^2 (1 + \cos^2 \theta) \quad (2)$$

In eqn. 2 π has its normal value, n is the refractive index of the solution, λ is the wavelength of light, N_A is Avogadro's number, (dn/dc) is the refractive index increment, and θ is the

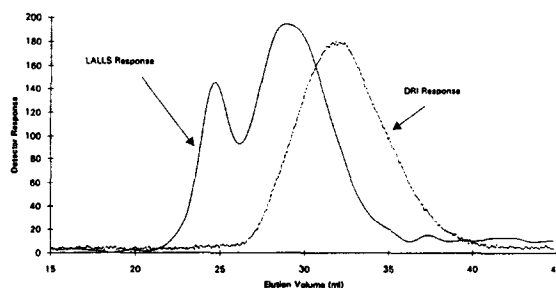


Fig. 1. DRI and LALLS detector responses for NBS 1476.

angle of the measurement. In low-angle laser-light scattering θ is typically less than 10 and $(1 + \cos^2 \theta)$ reduces to a value of two.

The molecular mass calculated from eqn. 1 for the data in Fig. 1 is 105 000 g/mol. This value is obviously low since at several of the early elution volumes the concentration is zero. A way to get a better approximation of the mass-average molecular mass of this sample is to use the method first described by Martin [23] (eqn. 3 below). In this method the total area of the LALLS detector response and the total concentration are used. The value obtained for the data in Fig. 1 by this method is 122 000 g/mol. Although the value here is higher it is still much lower than the value found for static light scattering for NBS 1476.

$$M_w = \frac{k_c}{Kk_{LS}} \cdot \frac{\text{total peak area of the LALLS signal}}{\text{total peak area of the DRI signal}} \quad (3)$$

Here k_c is the proportionality constant between the signal of the DRI detector and the concentration, k_{LS} is the similar constant for the LALLS detector signal, and K is defined in eqn. 2 above. A potential disadvantage of this equation is that the second virial coefficient cannot be used since the concentration is not calculated at each elution volume. This is not a problem for polyethylene, however, since the value of the second virial coefficient in TCB is so low [12].

Another problem which we have experienced is specific to high-molecular-mass, high-density polyethylenes (HMW-HDPEs). This problem is best described as a lack of reproducibility and a large amount of spiking as shown in Fig. 2 and Table III. Fig. 2 shows the LALLS detector response for a typical HMW-HDPE sample run using the Polymer Labs.' 10- μ m columns and a 1.0 ml/min flow-rate. As can be seen, there is a tremendous amount of spiking present. The data in Table III were calculated using the area under the LALLS detector response for 5 samples run back to back. These data may actually be a little misleading, since they were smoothed and de-spiked before being reduced.

To address this problem, we began a study to evaluate several different column particle sizes

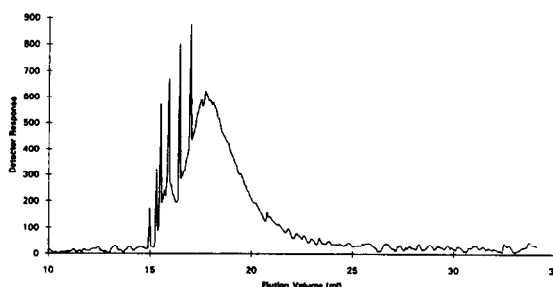


Fig. 2. LALLS detector response for HMW-HDPEs. Polymer Labs.' 10- μ m columns, 1.0 ml/min flow-rate.

and frit sizes to determine if the problems we were seeing with HMW-HDPEs were a result of shear degradation in the columns. Table I describes the samples used, Table II describes the columns used and Tables IV–VIII show the results of a flow-rate study using each of the column sets.

NBS 1475 was used as a standard to show that the instrument was operating properly. As indi-

TABLE III

GPC–LALLS REPRODUCIBILITY STUDY OF HMW-HDPE RESIN USING POLYMER LABS.' 10- μ m COLUMNS AND A 1.0 ml/min FLOW-RATE

Run	M_w
1	$2.36 \cdot 10^5$
2	$2.84 \cdot 10^5$
3	$2.56 \cdot 10^5$
4	$2.70 \cdot 10^5$
5	$2.50 \cdot 10^5$
R.S.D. (%)	7.1

TABLE IV

GPC–LALLS RESULTS ON THE POLYMER LABS.' 10- μ m GPC COLUMNS

Resin	M_w		
	1.0 ml/min	0.2 ml/min	0.1 ml/min
NBS 1475	$5.4 \cdot 10^4$	$5.33 \cdot 10^4$	$5.67 \cdot 10^4$
NBS 1476	$1.01 \cdot 10^5$	$1.34 \cdot 10^5$	$1.4 \cdot 10^5$
LDPE-A	$4.62 \cdot 10^5$	–	$4.77 \cdot 10^5$
LDPE-B	$2.7 \cdot 10^5$	–	$2.91 \cdot 10^5$
LLDPE-A	$1.25 \cdot 10^5$	–	$1.33 \cdot 10^5$

TABLE V

GPC-LALLS RESULTS ON POLYMER LABS.' 20- μ m PARTICLE SIZE COLUMNS WITH 10- μ m FRITS

Resin	M_w		
	1.0 ml/min	0.2 ml/min	0.1 ml/min
NBS 1475	$5.18 \cdot 10^4$	$5.21 \cdot 10^4$	$5.27 \cdot 10^4$
NBS 1476	$1.17 \cdot 10^5$	$1.58 \cdot 10^5$	$1.99 \cdot 10^5$
LDPE-A	$5.41 \cdot 10^5$	$5.51 \cdot 10^5$	$5.85 \cdot 10^5$
LDPE-B	$2.95 \cdot 10^5$	$3.05 \cdot 10^5$	$3.19 \cdot 10^5$
LLDPE-A	$1.25 \cdot 10^5$	$1.27 \cdot 10^5$	$1.23 \cdot 10^5$

TABLE VI

GPC-LALLS RESULTS ON POLYMER LABS.' 20- μ m PARTICLE SIZE COLUMNS WITH 5- μ m FRITS

Sample	M_w		
	1.0 ml/min	0.2 ml/min	0.1 ml/min
NBS 1475	$5.55 \cdot 10^4$	$5.43 \cdot 10^4$	–
NBS 1476	$1.20 \cdot 10^5$	$1.65 \cdot 10^5$	–

TABLE VII

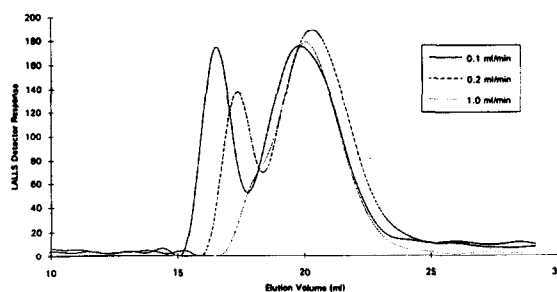
GPC-LALLS RESULTS ON PHENOMENEX 20- μ m PARTICLE SIZE COLUMNS WITH A 10- μ m FRIT

Sample	M_w		
	1.0 ml/min	0.2 ml/min	0.1 ml/min
NBS 1475	$5.2 \cdot 10^4$	–	–
NBS 1476	$1.09 \cdot 10^5$	–	–

TABLE VIII

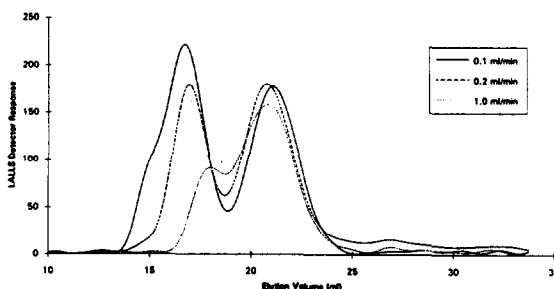
GPC-LALLS RESULTS FOR THE WATERS STYRAGEL COLUMNS

Resin	M_w		
	1.0 ml/min	0.2 ml/min	0.1 ml/min
NBS 1475	$6.1 \cdot 10^4$	$5.38 \cdot 10^4$	$5.7 \cdot 10^4$
NBS 1476	$1.95 \cdot 10^5$	$2.07 \cdot 10^5$	$2.77 \cdot 10^5$
LDPE-A	$6.32 \cdot 10^5$	$6.17 \cdot 10^5$	$6.25 \cdot 10^5$
LDPE-B	$3.64 \cdot 10^5$	$3.41 \cdot 10^5$	$3.55 \cdot 10^5$
LLDPE-A	$1.44 \cdot 10^5$	$1.37 \cdot 10^5$	$1.45 \cdot 10^5$

Fig. 3. LALLS detector response for NBS 1476. Polymer Labs.' 10- μ m columns.

cated in Tables IV–VIII, the mass-average molecular mass of NBS 1475 was consistently around 55 000 g/mol and was independent of the flow-rate or column set used. Conversely, the molecular mass of NBS 1476 varied dramatically with flow-rate and particle size of the column packing. This is shown in Figs. 3–5 and Tables IV, V and VIII. These data strongly suggest that NBS 1476 is shear degraded as it passes through the GPC columns, since the molecular mass is dependent on both particle size and flow-rate. Interestingly, in Fig. 5 there is an extra peak in the LALLS detector response around an elution volume of 11 ml. This is most likely totally excluded polymer. At the lower flow-rates this very-high-molecular-mass polymer has more time to diffuse into and out of void spaces and is retained a little, thus the peak does not appear at the lower flow-rates. It probably does not appear in the other smaller particle size column sets because it is shear degraded down to a smaller size.

Another interesting finding of this study was

Fig. 4. LALLS detector response for NBS 1476. Polymer Labs.' 20- μ m columns.

that the mass-average molecular mass of NBS 1476 was up around 280 000 g/mol. This is higher than had been found before. However, Stejskal *et al.* [4] found a molecular mass of 254 000 g/mol and suggested that the molecular mass could be higher because of errors which occur in extrapolating to zero concentration and angle in the Zimm plot.

Frit size did not seem to make a difference. This is demonstrated by comparing the molecular mass of NBS 1476 determined using the Polymer Labs.' 20- μm columns with 5- and 10- μm frit sizes. This seems reasonable since the post-column filter size is much smaller, *i.e.*, 0.5 versus 5 and 10 μm .

We also investigated two commercial low-density products and a linear-low-density product to determine if the molecular mass of these resins was affected by flow-rate. These samples are described in Table I and the molecular mass data are shown in Tables IV, V and VIII. The values show that varying the flow-rate had very little effect on the molecular mass of the LLDPE resin. There was an effect on the two LDPEs, however, it was much smaller than the effect on NBS 1476. The most likely explanation for this phenomenon is that these samples did not contain the small amount of very-high-molecular-mass polymer which NBS 1476 contains. It is this very-high-molecular-mass polymer or microgel which is sensitive to the shear degradation.

Another interesting finding of this flow-rate and particle size study was that the spiking found typically for HMW-HDPE resins disappeared when the flow-rate was at 0.2 ml/min or less. This finding was very exciting and allowed us to

TABLE IX

GPC–LALLS REPRODUCIBILITY STUDY USING WATERS' STYRAGEL COLUMNS WITH 0.1 ml/min FLOW-RATE

Run	M_w
1	$1.60 \cdot 10^6$
2	$1.57 \cdot 10^6$
3	$1.55 \cdot 10^6$
4	$1.63 \cdot 10^6$
5	$1.64 \cdot 10^6$
R.S.D. (%)	2.4

greatly improve the reproducibility of our molecular mass characterization of these resins. The results of a reproducibility study for the same sample shown in Fig. 2 and Table III are shown in Table IX. An overlay of the LALLS detector responses are shown in Fig. 6. As indicated in Table IX, the data at the lower flow-rates with the larger particle size columns is much more reproducible and the molecular masses are much higher. In the past spiking has been attributed to incomplete dissolution of HMW-HDPEs even though dissolution is carried out well above the melting point of the polymer [25]. The data here indicates that the spiking may be attributed to a chromatographic phenomenon, perhaps polarization as described by Giddings [19]. The polarization effect could cause high molecular mass polymer to concentrate and thus come out of solution.

The results of this study indicate that there is severe shear degradation occurring during the passage of NBS 1476 through smaller particle size GPC columns. This finding successfully

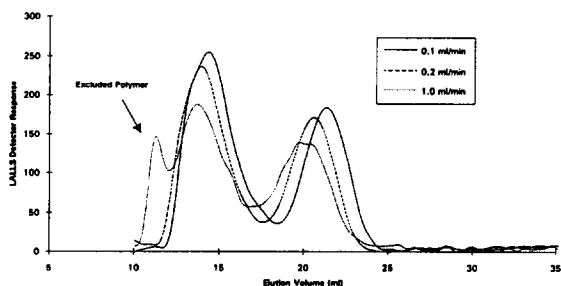


Fig. 5. LALLS detector response for NBS 1476. Waters' Styragel columns.

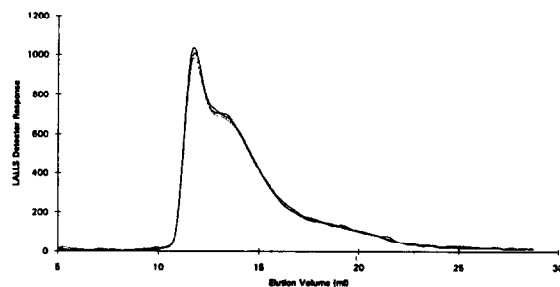


Fig. 6. LALLS detector response for HMW-HDPE. Waters' Styragel columns, 0.1 ml/min flow-rate.

explains the discrepancy which has existed in the literature for several years between the molecular mass of NBS 1476 determined using the GPC-LALLS technique and the molecular mass determined using static light scattering. This finding will also allow us to determine more accurate molecular masses for higher-molecular-mass polyethylenes. Finally, a method was developed which allows us to characterize the molecular mass of HMW-HDPEs.

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