Measurement of the Absolute Molecular Weight and Molecular Weight Distribution of Polyolefins using Low-Angle Laser Light Scattering

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Synopsis

By connecting a low-angle laser light scattering photometer (LALLSP) on line with a high-temperature gel permeation chromatograph (GPC), molecular weight distributions were determined for three polyethylene standards (two high density and one low density) without resorting to column calibration procedures. In addition, the absolute weight-average molecular weight and second virial coefficients of four polyethylene standards (three high density and one low density) were obtained using low-angle laser light scattering. The molecular weights measured were in excellent agreement with those specified by the National Bureau of Standards. For the low density material, a microgel fraction was detected by the on-line LALLSP but not by the conventional GPC detector. This resulted in a z-average molecular weight of over 3×10^6 daltons, an order of magnitude greater than that determined by conventional GPC techniques.

INTRODUCTION

Conventional methods of determining the molecular weight distribution of polyolefins by gel permeation chromatography[1-4] (GPC) require the calibration of the instrument with well characterized standards of low polydispersity. When standards of the same composition as the polymers to be analyzed are available, then a calibration curve of the logarithm of the molecular weight versus elution volume can be used. If the polymers to be analyzed have different compositions than the standards, universal calibration procedures[4-6] must be used. Even universal calibration can yield erroneous results if the calibrants and standards have different degrees of branching or if branching is a function of molecular weight. Furthermore, changes in flow rate, temperature, or column characteristics can invalidate prior calibrations.

With the advent of a low-angle laser light scattering photometer (LALLSP), it has been demonstrated by Ouano[7] and Ouano and Kaye[8] that absolute molecular weight distributions can be determined without recourse to calibration procedures. However, the Ouano experiments were performed at room temperature and not at the elevated temperatures required for the characterization of polyolefins.

In this report we describe a technique for the determination of polyolefin molecular weight distributions by operating a LALLSP in conjunction with a high-temperature GPC. The stand-alone laser light scattering characterization of polyolefins is also described. The latter technique provides the absolute weight-average molecular weight and the second virial coefficients of the polymer.

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THEORY

The quantity of interest in light scattering measurements is the Rayleigh factor R_θ, defined by

$$R_\theta = J_\theta(I_0 V) \tag{1}$$

where J_θ is the radiant intensity (W/s) scattered at angle θ with respect to the illuminating beam of irradiance I_0 (W/cm^2), and V is the scattering volume. With the LALLSP used in this study the Rayleigh factor can be calculated from

$$R_\theta = (G_\theta/G_0)\,(D/\sigma'l') \tag{2}$$

Where G_θ and G_0 are the photomultiplier signals for the scattered and incident beam respectively, D is the transmittance of the measuring attenuators employed in the determination of G_0, σ' is the solid angle over which the scattered light is collected, and l' is the length of the scattering volume, parallel to the incident beam. Since D, σ', and l' are measurable instrument constants, the LALLSP gives R_θ without recourse to arbitrary standards.[9–11]

At the low forward scattering angles accessible with the LALLSP and at low solute concentration, the Rayleigh factor and the physical characteristics of the scattering polymer are related as

$$Kc/\overline{R}_\theta = 1/M_w + 2A_2c \tag{3}$$

where

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

and c is the concentration of the polymer in g/ml, $\overline{M}_w$ is the weight-average molecular weight, n is the refractive index of the solution, λ is the wavelength in vacuo, N is Avogadro's number, and A_2 is the second virial coefficient. The differential index of refraction, dn/dc, is the change in refractive index of the solution as a function of polymer concentration. The quantity $\overline{R}_\theta$ is the excess Rayleigh factor and is given simply by

$$\overline{R}_\theta = R_{\theta-\text{(solution)}} - R_{\theta-\text{(solvent)}} \tag{5}$$

Because of the low-angle capability of the LALLSP, the angular extrapolations (Zimm plots) employed in classical (wide-angle) light scattering are not required. To calculate $\overline{M}_w$, measurements of $\overline{R}_\theta$ are obtained for a few solutions of different c. As given by eq. (3), a simple plot of $Kc/\overline{R}_\theta$ vs. c yields $(\overline{M}_w)^{-1}$ as the intercept and $2A_2$ as the slope.

It is the low-angle capability of the LALLSP which also allows it to be used as an on-line detector for molecular weights. If the LALLSP is connected in series with the GPC columns and a suitable concentration detector (e.g., infrared or differential refractometer), then the molecular weight for uniform intervals on the elution curve is given by

$$M_i = (Kc_i/\overline{R}_{\theta,i} - A_ic_i)^{-1} \tag{6}$$

where $A_i = 2A_{2,i}$. The concentration c_i may be calculated directly from the amplitude x_i of the concentration detector, if the detector is calibrated. Generally it is more convenient to normalize the detector response as follows:

$$c_i = mx_i/V_i\Sigma x_i \tag{7}$$

where m is the mass injected, V_i is the effluent volume passing through the sample cell during the ith interval, and Σx_i is the sum of the x_i values for all the intervals within the peak.

The virial coefficient term A_i can be obtained from static analysis of the sample by determining the slope of a plot of $Kc/\overline{R}_\theta$ vs c. For most samples, the average value of A_i so obtained from a single analysis of the unfractioned sample can be applied to the entire distribution. Although it was not incorporated in this study, high-precision measurements on samples with wide distributions require that the variation of A_i with molecular weight be considered.[7]

Once M_i has been calculated at uniform intervals on the elution curve, the molecular weight averages may be calculated in the conventional manner, namely,

$$\overline{M}_n = \Sigma c_i / \Sigma(c_i/M_i) \tag{8}$$

$$\overline{M}_w = \Sigma c_i M_i / \Sigma c_i \tag{9}$$

$$\overline{M}_z = \Sigma c_i M_i^2 / \Sigma c_i M_i \tag{10}$$

As noted by Ouano,[7] the polydispersity index $\overline{M}_w/\overline{M}_n$ obtained by LALLSP/GPC analysis will be less than the true value. Due to the finite resolution of the GPC column, the M_i values do not represent monodisperse fractions. Instead, since the M_i values were determined by light scattering, they are weight-average values for the solute mixture eluting at a given time. Thus, as column resolution decreases, the calculated $\overline{M}_n$ will approach $\overline{M}_w$. Conversely, as the column resolution increases, the calculated $\overline{M}_n$ approaches the true value. However, $\overline{M}_w$ remains an absolute quantity. Conventional GPC results yield a $\overline{M}_w/\overline{M}_n$ ratio greater than the true value unless correction for axial dispersion (band broadening) is applied.[12] In a recent study of dextrans, Basedow et al.[13] reported that LALLSP/GPC provided polydispersity indices within 1.3% of GPC results corrected for band broadening, while the uncorrected GPC results erred by as much as 20%.

EXPERIMENTAL

All light scattering measurements were performed with the commercially available KMX-6 (Chromatix, Inc., Sunnyvale, Calif.) low-angle laser light scattering photometer using the standard high-temperature sample cell. The KMX-6 incorporates a He-Ne laser source ($\lambda = 6328$ Å). For the static measurement of $\overline{M}_w$ and A_2, polyethylene solutions were prepared on a volumetric basis (g/ml) at 135°C in 1,2,4-trichlorobenzene (practical grade J. T. Baker). Solutions were then introduced by syringe into the heated (135°C) sample cell. Once the cell was purged with a new solution, the flow was stopped and the solution allowed to thermally equilibrate (less than one minute) before measurements were made. A complete set of data, such as shown in Figure 1, was obtained in less than 2½ hr. More than 50% of this period was sample preparation and dissolution time.

Although the small scattering volume of the KMX-6 LALLSP significantly reduced the sensitivity of the light scattering measurements to particulate contamination, improved signal-to-noise conditions were obtained by filtering the sample solution between the syringe and the cell. Both the syringe and the
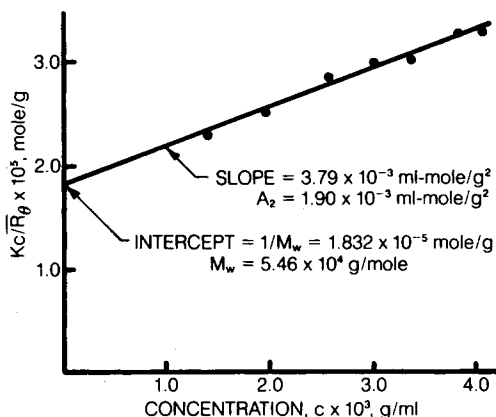
Fig. 1. $Kc/\overline{R}_\theta$ vs c plot for static analysis of SRM 1475 in TCB at 135°C.

filter housing were heated to approximately 145°C. An 0.5 μm Fluoropore (Millipore Corp.) filter was utilized. The Fluoropore filter consisted of a Teflon membrane on a polyethylene grid. At the specified conditions, the polyethylene grid softened over a period of one to several hours. With the grid faced toward the syringe the polyethylene eventually clogged the membrane filter. However, the polyethylene did not otherwise affect the analysis. (Faced toward the sample cell, the degrading grid caused a high particulate noise level.) Repeated measurements of R_θ for hot solvent passed through the filter indicated no increase due to extracted polyethylene.

The GPC utilized in the LALLSP/GPC measurements incorporated a high thermal mass aluminum oven, a modified Model 6000A (Waters Associates, Milford, Mass.) solvent delivery system and a six-loop injection system (Valco, Inc., Houston, Tex.) with pneumatically controlled valves built into the oven. A modified Miran I (Wilks, S. Newark, Conn.) infrared detector with a 3.41 μm narrow bandpass filter was used as the concentration detector. Five Styragel columns of porosities 10^7, 10^5, 10^4, 10^3, and 60 Å were connected in series. The solvent was 1,2,4-trichlorobenzene and the operating temperature of the oven and the infrared cell was 135°C.

The LALLSP was mounted on top of the oven and was connected between the column and the infrared detector using 0.009-in.-i.d. stainless-steel tubing. A low-volume filter cartridge containing a 0.2 μm Fluoropore filter was placed between the columns and the LALLSP cell. The polyethylene filter grid was extracted by the solvent in a few hours. The cell, filter, and connecting tubing were maintained at 135°C.

For this portion of the study, samples were accurately prepared at room temperature on a w/w basis (0.6 to 1.2% w/w), and the w/v concentration at 135°C was then calculated based on the known change in solvent density. The dissolved solutions were subsequently loaded into the injection loops and injected under programmer control. The analog response data from both detectors were obtained on a strip chart recorder, together with "pip" marks corresponding to 5 ml siphon dumps. The analog data were manually digitized and the molecular weight averages were calculated with a PDP-1140 minicomputer program.

Values of the differential index of refraction, dn/dc, in TCB were obtained with a precision differential refractometer utilizing a laser source (λ = 6328 Å)

TABLE I
M_w and A_2 Values for Polyolefins in 1,2,4-Trichlorobenzene at 135°C

Sample	A_2, ml/g[a]	LALLSP[b]	NBS[c]	Ref. 4[d]
SRM 1475	$(1.90 \pm 0.10) \times 10^{-3}$	$54,600 \pm 1100$	$52,500 \pm 1800$	—
SRM 1483	$(1.71 \pm 0.07) \times 10^{-3}$	$32,600 \pm 700$	$32,100 \pm 700$	—
SRM 1484	$(1.34 \pm 0.17) \times 10^{-3}$	$118,000 \pm 3000$	$119,600 \pm 2200$	—
SRM 1476	$(4.3 \pm 0.6) \times 10^{-4}$	$221,000 \pm 9000$	—	140,000

[a] Uncertainties given are standard deviations of the regression coefficients (A_2) calculated for the data shown in Figures 1–4.

[b] Uncertainties given are estimated standard deviations based on one measurement on each of the solutions indicated in Figures 1–4. Uncertainty introduced in the initial solute concentration is included, but uncertainty due to interpellet variability in SRM 1475 and SRM 1476 is excluded.

[c] Uncertainties given are standard deviations of multiple analyses (precision) as specified by NBS. Accuracy error of the conventional light scattering measurements is not included.

[d] By classical light scattering after Celite column clarification.

and a digital readout of the angular displacement. This instrument was a prototype of a commercially available instrument (Model KMX-16, Chromatix, Inc.). Multiple measurements were made in solutions of 1 to 5 mg/ml and dn/dc was taken as the value of $\Delta n/\Delta c$ extrapolated to $c = 0$. To assess the sensitivity of the measurement in various solvents, dn/dc was also measured in orthodichlorobenzene (ODCB) and α-chloronaphthalene (α-ClN).

RESULTS AND DISCUSSION

The weight-average molecular weights and second virial coefficients of SRM 1475, SRM 1483, SRM 1484 [all high-density polyethylene (HDPE)], and SRM 1476 (low-density polyethylene (LDPE)] determined by off-line (static) light scattering experiments are given in Table I. The $Kc/\overline{R}_\theta$ vs c plots for the analyses are shown in Figures 1 through 4. The dn/dc values used in the calculations are
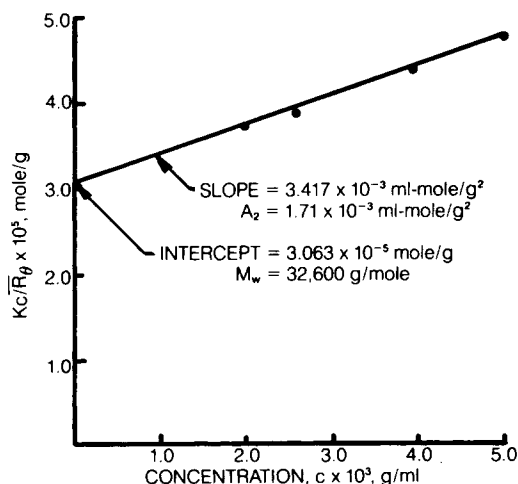

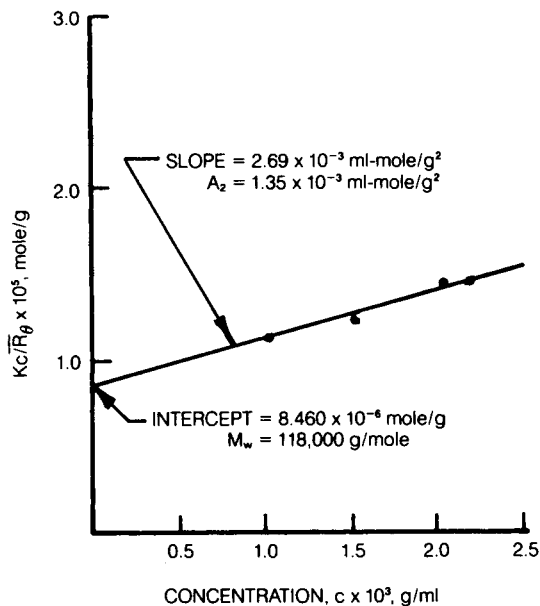Fig. 2. $Kc/\overline{R}_\theta$ vs c plot for static analysis of SRM 1483 in TCB at 135°C.

Fig. 3. $Kc/\overline{R}_\theta$ vs c plot for static analysis of SRM 1484 in TCB at 135°C.
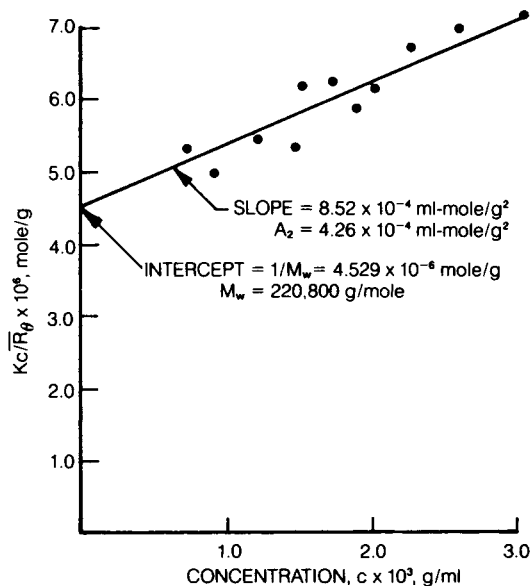

Fig. 4. $Kc/\overline{R}_\theta$ vs c plot for static analysis of SRM 1476 in TCB at 135°C.

among those listed in Table II. The $\overline{M}_w$ values determined for the high-density standards are in excellent agreement with those obtained by NBS using conventional light scattering techniques requiring significantly more experimental

TABLE II
Values of dn/dc for High-Density and Low-Density Polyethylene

Sample	Solvent	Temperature, °C	dn/dc, ml/g (λ = 6328 Å)
SRM 1475	TCB	135	-0.104 ± 0.001
SRM 1475	ODCB	135	-0.056 ± 0.002
SRM 1476	TCB	135	-0.091 ± 0.002
HDPE	α-ClN	145	-0.177 ± 0.002

work. The second virial coefficients for the two narrow standards SRM 1483 and 1484 show only a slight decrease with increasing molecular weight. The A_2 value for SRM 1475 is higher than expected, possible due to the polydispersity of the sample. The presence of considerable low-molecular-weight material will increase A_2.

For SRM 1476 (LDPE), the weight-average molecular weight measured with the LALLSP was considerably larger than that obtained by Wagner and McCrackin.[4] For their measurements the sample was clarified by passing it through a Celite column. A sample filtered in this manner would be expected to yield a lower $\overline{M}_w$ due to the removal of some of the high-molecular-weight material by the column. Other classical light scattering studies performed without such clarification led to considerable curvature in the Zimm plots, which is indicative of high-molecular-weight gel.[14,15] Polymer particulates in LDPE samples have also been identified by electron microscopy.[16] Since the LALLSP operates at very low angles, the Zimm plot was linear in the investigated concentration range. Only a simple filtration to remove dust was required to obtain a valid $\overline{M}_w$ for the LDPE sample. However, as seen in Figure 4, the uncertainty of the LDPE analysis was greater than for the HDPE analyses. This is thought to have resulted from a slight, varying retention of the high-molecular-weight fraction, by the sample cell filter, as evidenced by its gradual clogging.

The raw strip chart results for LALLSP/GPC measurements performed on two high-density polyethylene standards (SRM 1484 and SRM 1475) and one low-density polyethylene standard (SRM 1476) are shown in Figures 5 to 7. Analysis conditions are given in the figure captions.

The two detector responses (LALLSP and infrared) are similar for the two HDPE standards, but very different for the LDPE standard. The first peak in the LALLSP chromatogram for SRM 1476 (Fig. 7) occurs without detectable infrared response. This indicates trace amounts of very high-molecular-weight polymer, corroborating the static results. Due to the high sensitivity of the KMX-6 to high-molecular-weight species[17] it may be used to detect microgels at concentrations far below the detection limit of the infrared detector. The second broad peak is the type of response one would expect if no gel was present.

The number-average, weight-average, and z-average molecular weights were calculated from these chromatograms using eqs. (6) through (10). The results are given in Table III. The dn/dc and A_2 values used are those presented in Tables I and II. We did not include molecular weight variations in dn/dc or A_2. Calculations were also performed with the second virial coefficient set equal to zero. Only a 2% to 5% error is incurred by neglecting the second term in eq. (6), with the resultant molecular weights being lower. Thus for many applications
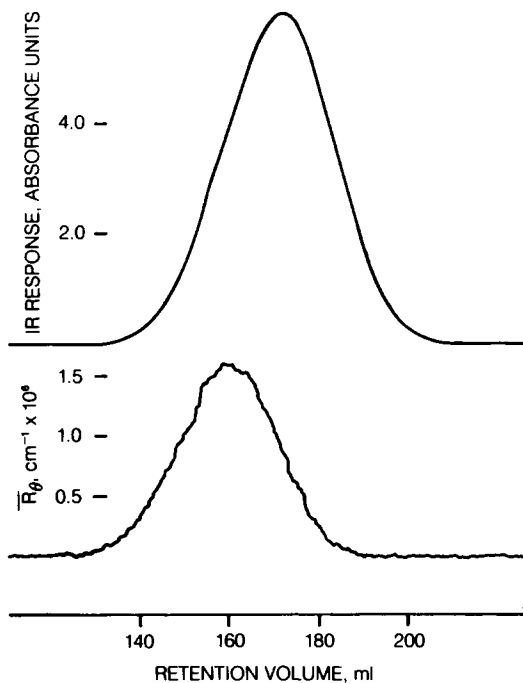
Fig. 5. LALLSP/GPC chromatogram of SRM 1475 in TCB at 135°C. The units on the LALLSP response have been converted from G_θ to $\bar{R}_\theta$ units according to eqs. (2) and (5). Analysis conditions: flow rate, 2.138 ml/min; mass injected, 9.2 mg; $K = 9.953 \times 10^{-8}$ mole cm^2/g^2; $G_0 = 717$; $A_2 = 1.9 \times 10^{-3}$ ml mole/g; R_θ solvent $= 3.52 \times 10^{-5}$ cm^{-1}; injection loop, 0.5 ml.

it may not be necessary to determine A_2 before performing LALLSP/GPC measurements.

The LALLSP/GPC results for the two high-density polyethylene standards are in excellent agreement with those listed by NBS. The number-average and weight-average molecular weights calculated for LDPE (SRM 1476) are also in good agreement with those reported by Wagner and McCrakin.[4] The discrepancy between the LALLSP and the LALLSP/GPC $\bar{M}_w$ values for SRM 1476 apparently resulted from the loss of high-molecular-weight polymer on the GPC column, as discussed above for the Celite column, and/or the low sensitivity of the IR detector to the high-molecular-weight fraction.

The $\bar{M}_z$ value for SRM 1476 is an order of magnitude greater than that obtained by conventional GPC. This results from the very high-molecular-weight fraction, which is not detected by the GPC detector, and suggests that many z-average molecular weights for LDPE obtained by conventional GPC techniques are probably incorrect. However, the LALLSP/GPC value for $\bar{M}_z$ must be interpreted qualitatively, due to the high uncertainty in the concentration. For example, a second analysis of SRM 1476 led to a $\bar{M}_z$ value of only 3.6 million instead of 12.4 million. The $\bar{M}_n$ and $\bar{M}_w$ were within 6% of the first run. Therefore, only a qualitative value for $\bar{M}_z$ is given in Table III.

It should be noted that LALLSP/GPC measurements require strict quantitative procedures whereas normal GPC runs do not. Both the mass injected (i.e.,

TABLE III
Molecular Weights Obtained for HDPE and LDPE by LALLSP/GPC Analysis

Sample	LALLSP/GPC[a]			NBS			Ref. 4[b]	
	M_n	M_w	M_z	M_n	M_w	M_z	M_n	M_w
SRM 1475	19,000	55,800	162,000	18,300[c]	52,500[d]	149,000[e]		
SRM 1484	99,700	109,500	125,600	100,500[f]	119,600[g]	N.A.[h]		
SRM 1476	28,000	100,400	$>3 \times 10^6$				25,000	105,000

[a] See text for probable accuracy error.
[b] By GPC using sum of fractions calculation.
[c] By GPC, estimate of precision ± 1200, estimate of systematic error not available.
[d] By light scattering, estimate of precision ± 1800, estimate of systematic error not available.
[e] By GPC, estimate of precision ± 13000, estimate of systematic error not available.
[f] By membrane osmometry, standard deviation 3.7%, expected limit of systematic error 4%.
[g] By light scattering, standard deviation 1.8%, expected limit of systematic error 11%.
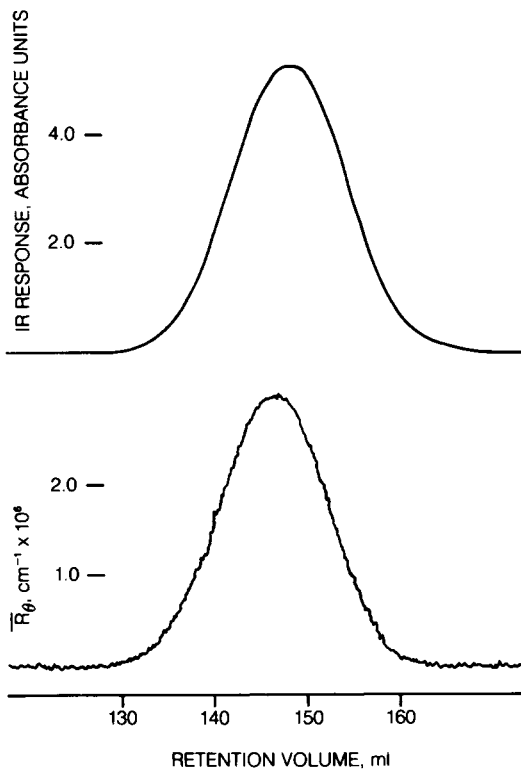[h] N. A. denotes not available.

Fig. 6. LALLSP/GPC Chromatogram of SRM 1484 in TCB in 135°C. Analysis conditions: flow rate, 1.03 ml/min; mass injected, 3.87 mg; $A_2 = 1.35 \times 10^{-3}$ ml mole/g; other conditions as in Figure 5.

sample concentration and loop volume) and the flow rate must be known accurately. If data are taken from the strip-chart output, the chart speed must also be known. For the feasibility studies carried out here, little effort was made to minimize the error in these parameters. Propagation of the estimated uncertainty in each of these parameters yielded an overall uncertainty in $\overline{M}_w$ of nearly 10%, primarily due to uncertainty in the loop volume and paper slippage in the recorder. However, with accurate values for the above parameters, the inherent uncertainty of a LALLSP/GPC analysis is approximately 2.5% for $\overline{M}_w$, not including error in the dn/dc measurements.

The techniques reported herein may be readily extended to other polyolefins and/or solvents. However, the sensitivity of the light scattering response, and thus the precision of the analysis will be highly dependent on the solvent utilized. As given by eqs. (3) and (4), the light scattering response is proportional to the term $(dn/dc)^2$. From the data in Table II, it is seen that light scattering experiments in TCB will be 3.45 times more sensitive than in ODCB. Similarly, a nearly threefold gain in sensitivity over TCB can be obtained by using α-ClN. However, α-ClN is not a good infrared solvent at 3.41 μm. Also, some investigators have reported aggregation of polyethylene in α-ClN,[18,19] while others have
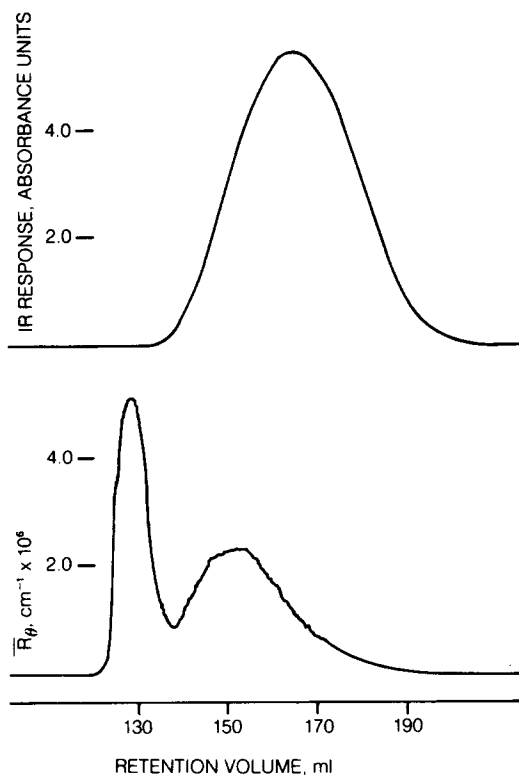
Fig. 7. LALLSP/GPC Chromatogram of SRM 1476 in TCB at 135°C. Analysis conditions: flow rate, 2.138 ml/min; mass injected, 9.28 mg; $A_2 = 4.26 \times 10^{-4}$ ml mole/g; other conditions as in Figure 5.

refuted this observation.[20] ODCB is a good infrared solvent but the low dn/dc value would require an impractically high concentration for the injected sample. Thus, with an infrared detector, TCB is the solvent of choice. When a differential refractometer is employed, α-ClN will provide enhanced sensitivity for both the light scattering and concentration detectors.

CONCLUSIONS

A low-angle laser light scattering photometer has been connected to a high-temperature gel permeation chromatograph and the absolute molecular weight distribution of polyolefins determined. Excellent agreement with the NBS values was found for the number-average and weight-average molecular weights of the high-density and low-density standards employed in this study.

Small amounts of microgel in the LDPE SRM 1476 material caused a significant LALLSP detector response and resulted in a very large z-average molecular weight. This high molecular weight fraction has not been previously detected using conventional GPC analysis due to the very small amounts present.

Stand-alone low-angle laser light scattering measurements of three high-

density polyethylenes yielded weight-average molecular weights in agreement with NBS values. A similar analysis of the low-density standard yielded a weight-average molecular weight significantly higher than literature data, due to presence of microgel that had been removed in the previous study.

References

1. G. Ross and L. Frolen, *J. Res. Natl. Bur. Stand.*, **76A**, 163 (1972).
2. N. Nakajima, *Adv. Chem.*, **125**, 98 (1973).
3. J. H. Ross, Jr. and R. L. Shank, *Adv. Chem.*, **125**, 108 (1973).
4. H. L. Wagner and F. L. McCrackin, *J. Appl. Polym. Sci.*, **21**, 2833 (1977).
5. E. E. Drott and R. A. Mendelson, *J. Polym. Sci.*, *A-2*, **8**, 1361 (1970).
6. H. Benoit, Z. Grubisic, and P. Rempp, *J. Polym. Sci.*, *Part B*, **5**, 753 (1967).
7. A. C. Ouano, *J. Chromatogr.*, **118**, 303 (1976).
8. A. C. Ouano and W. Kaye, *J. Polym. Sci.*, **12**, 1151 (1974).
9. W. Kaye and A. J. Havlik, *Appl. Opt.*, **12**, 541 (1973).
10. W. Kaye, *J. Colloid Interface Sci.*, **46**, 543 (1974).
11. W. Kaye and J. B. McDaniel, *Appl. Opt.*, **13**, 1934 (1974).
12. T. Kotaka, *J. Appl. Polym. Sci.*, **21**, 501 (1977).
13. A. Basedow, *Deutsche Diskussionstagung fur Anwendug der HPLC*, Vol. 2, Waters Associates, Konigstein/Tannus FRG, 1977, pp. 175–200.
14. L. D. Moore, *J. Polym. Sci.*, **20**, 137 (1956).
15. L. T. Muus and F. W. Billmeyer, Jr., *J. Am. Chem. Soc.*, **79**, 5079 (1957).
16. L. D. Moore and V. G. Peck, *J. Polym. Sci.*, **26**, 141 (1959).
17. A. C. Ouano, *J. Colloid Interface Sci.*, **63**, 275 (1978).
18. Q. A. Trementozzi, *J. Polym. Sci.*, **36**, 113 (1959).
19. H. P. Schreiber and M. H. Waldmen, *J. Polym. Sci.*, **A2**, 1655 (1964).
20. V. Kokle, F. W. Billmeyer, Jr., L. T. Muus, and E. J. Nwitt, *J. Polym. Sci.*, **62**, 251 (1962).